East Engin. Library
TX
341
F69
V.5
No.6

FOOD TECHNOLOGY

PUBLISHED BY THE INSTITUTE OF FOOD TECHNOLOGISTS

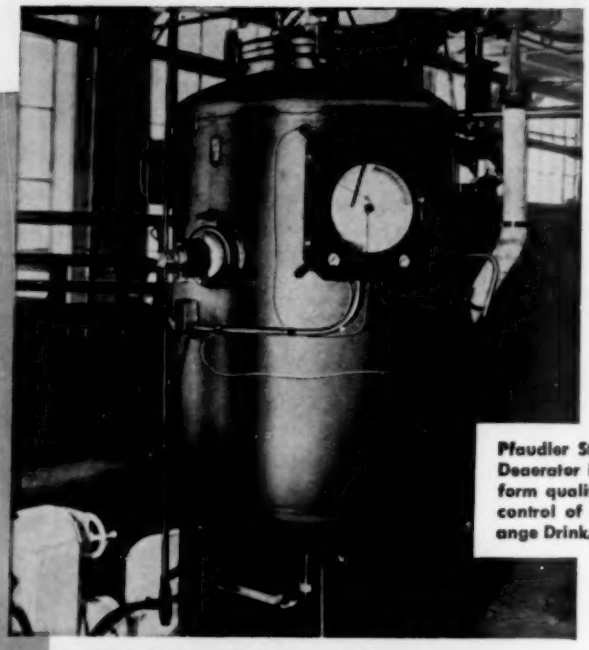
June 17-21 ELEVENTH ANNUAL MEETING New York

Volume 5, Number 6
June, 1951

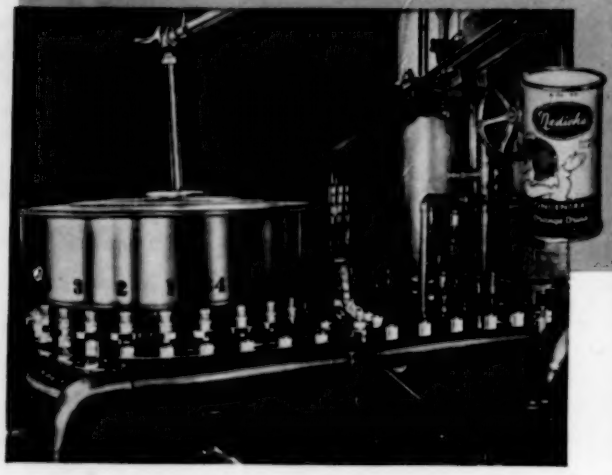
UNIVERSITY OF MICHIGAN LIBRARIES

How Pfaudler Equipment Aids Nedicks

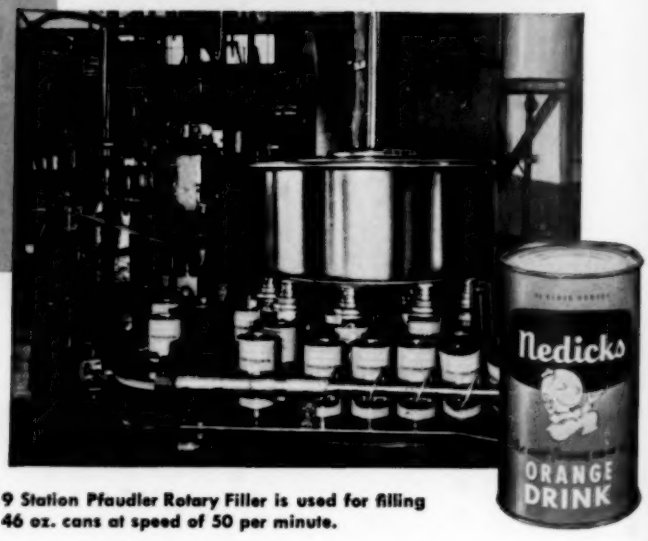
to process quality orange drink



Pfaudler Stainless Steel Deaerator is key to uniform quality and flavor control of Nedick's Orange Drink.



24 Station Pfaudler Rotary Filler where 6 oz. cans are filled at a rate up to 400 per minute.



9 Station Pfaudler Rotary Filler is used for filling 46 oz. cans at speed of 50 per minute.

Nedick's is a famous name in orange drinks, and by producing a *uniformly* good quality of orange concentrate, demand has increased phenomenally. How do they do it? The answer—fast processing!

This orange product, like all citrus juices, is quick to oxidize. Nobody wants your product after that. With the aid of a Pfaudler deaerator in combination with Pfaudler High-Speed Rotary Fillers, Nedick's has solved the problem of oxidation.

The deaerator removes the air which is so detrimental to flavor and keeping quality, just before the product is canned. A constant vacuum is maintained as juice flows through the unit. According to Mr. E. S. Hansen, Production Manager of Nedick's, ". . . tests for residual air content in the product demonstrate efficient deaeration." Result—good flavor.

Speed of handling is also essential—the reason why Nedick's uses one 9 Station Pfaudler Filler for handling 46 oz. cans and one 24 station machine for filling 6 oz. cans. These machines are noted for their speed as well as their accurate and clean fill. When you can pack as good a product as Nedick's Orange Drink base day after day, isn't it good proof of the profitability of using Pfaudler equipment and process know-how?

Pfaudler

THE PFAUDLER CO., ROCHESTER 3, NEW YORK

Engineers and Fabricators of Food Processing Equipment

GLASS LINED STEEL
Hastelloy · Aluminum
Tantalum · Carbon Steel
Solid or Clad Stainless Steel
Nickel · Inconel · Monel

For full details
on Pfaudler Food Processing Equipment
see the Pfaudler Representative at

BOOTH 3

INSTITUTE OF FOOD TECHNOLOGISTS

11th Annual Meeting

June 17-20 **Hotel New Yorker**

Fundamentals of Freeze-Concentration of Liquids

RUDOLF HEISS AND LISELOTTE SCHACHINGER

Institute of Food Technology, Munich, Germany

(Received for pu' lication August 1, 1949)

The fundamentals involved in computing maximum obtainable concentrations and yields by freeze-concentration of aqueous solutions are discussed. Crystallization rates, number of nuclei, and recrystallization are described and illustrated by microphotographs. Data obtained by the rotating drum technique of freeze-concentration are presented to show the effects of various conditions.

In the freezing of aqueous solutions, an increased separation of pure ice occurs with decreasing temperature, and the remaining solution is thereby concentrated. Because this process was recognized as one of the causes of irreversible changes appearing in the colloidal system of foods, it has been studied intensively *(6)*. While the freezing of water in foods causes colloidal and enzymic changes which may have a harmful effect, the process of freezing solutions can be successfully used in concentrating the liquid phase. An extensive substitution of freeze-concentration for evaporation-concentration was originally expected because heat of fusion of ice is lower than the heat of evaporation of water. However, it became clear in the course of time that the higher costs of one calory of "cold" and of refrigeration equipment have limited the general use of freeze-concentration. The method may be practical, however, with solutions which tend to foam, such as protein-containing soya milk and beer. Its main importance probably lies in the concentration of solutions containing traces of aromatic substances which have very low boiling points. In the evaporation process, these substances are only partially recovered by involved processes. Examples of such products include extracts of herbs, delicately flavored fruit juices and coffee extracts.

Information which is available on the technique of freeze-concentration, on the choice of temperatures, and on the resulting yield and concentrations, is limited. For this reason, these factors will be discussed here in detail.

THEORETICAL PROCESS

A solution with concentration x_a, separates at the temperature t_f into a more concentrated solution x_f, and pure ice, x_0 (Figure 1). An initial unit weight of the solution splits into an ice component, m, and a new solution component, 1-m, and thus we have the following equation: $x_a \cdot 1 = x_0 \cdot m + x_f (1 - m)$. Since x_0 is zero (pure ice contains no solute), the water frozen out per kg. of initial solution (by solving above equation for m) is: $m = 1 - x_a/x_f$. The amount of concentrate per kg. of initial solutions is: $g_i = 1 - m = x_a/x_f$. The concentration ratio, k, is therefore $1/g_i$, or x_f/x_a. Thus the concentrate yield is inversely proportional to the concentration ratio.

The concentrate yield per kg. of initial water content is: $x_a/x_f(1 - x_a)$. While the concentrate yield per kg. of initial solids equals $1/x_f$. The final concentration attainable from a particular aqueous solution depends entirely upon the temperature (Figure 2). At a given temperature the theoretical concentrate yield of a particular aqueous solution depends exclusively on the initial concentration, x_a. The higher content of solids in the initial juice, the larger is the concentrate yield at constant temperature. On the other hand, the yield from a given initial concentration is greater, the higher the chosen freezing temperature. In the latter case, the concentrate, x_f, will be more dilute.

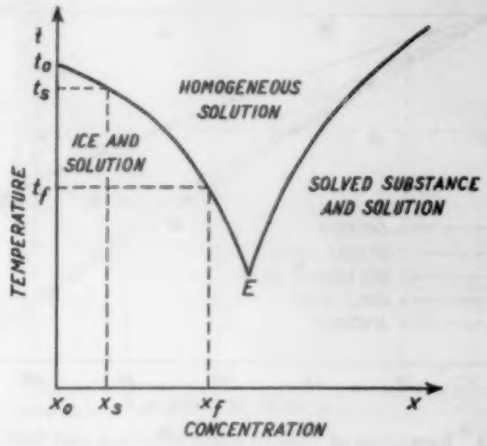


FIG. 1. Schematic drawing of a melting diagram of an aqueous solution.

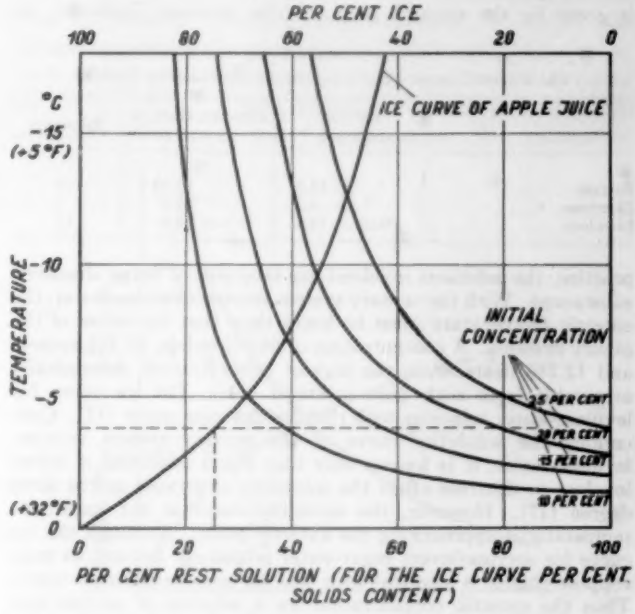


FIG. 2. Ice curve and concentrate yield of apple juice at different initial concentrations.

For example, to obtain a final concentration of 25% in the concentrate at −3.6° C. (21.5° F.), from original dilutions of 7.5, 10, 12.5 and 15%, theoretical yields of 30, 40, 50 and 60%, respectively, must be obtained. The amount of water which has to be separated is 70, 60, 50 and 40%, and the corresponding concentration ratios, x_f/x_a, are 3.3, 2.5, 2, and 1.67, respectively. The freezing curves of different sugar solutions and juices are compared in Figure 3. The ice curves for apple juice and red currant juice show close agreement with the data obtained by Riedel (15). We have no comparable data for orange juice. The

flatter courses of the orange juice curve can be explained by the higher proportion of sucrose (50 to 60% of the sugar). Other fruit juices contain more monosaccharides (3). The nearer the curve is to the horizontal (sucrose), the larger are the dry matter changes with temperature variations of a given magnitude. Consequently, the effect of unavoidable fluctuations in the process temperature will be accentuated, making freeze-concentration less suitable for such solutions.

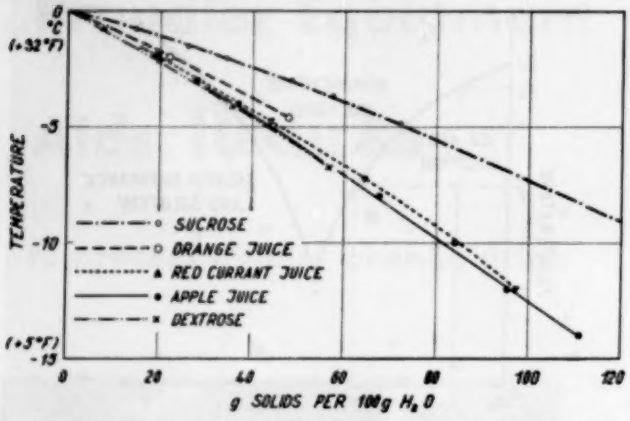


FIG. 3. Ice curves of various sugar solutions and fruit juices. The curves for sucrose, orange juice, and dextrose are from references 10, 15, and 7, respectively.

The highest concentration theoretically attainable by freezing is given by the eutectic point of the solution (Table 1). In practice, the solutions involved are mixtures of many dissolved substances. With the ternary system sucrose-dextrose-water, the eutectic temperature must be lower than that for either of the binary systems. A concentration of 64.9% solids, 52.2% sucrose and 12.7% dextrose, is the highest concentration theoretically attainable from such pure solutions (11). The ice curve for levulose-water coincides with that for dextrose-water (12). Concerning the solubility curve of the ternary system sucrose-levulose-water, it is known only that equal additions of either levulose or dextrose affect the solubility of sucrose to the same degree (17). However, the solubility curve is not known at temperatures approaching the eutectic point. Although the ice curve for sucrose-invert sugar-water is also not known, we may suppose that it is identical with that for sucrose-dextrose-water. Thus the eutectic concentration for a solution of sucrose and invert sugar is about 68% solids at −21° C. (−6° F.). This corresponds to a mixture of 21% invert sugar and 47% sucrose (8).

TABLE 1

The Highest Concentrations Theoretically Obtainable by Freezing

	Eutectic temperature, °C.	Concentration at the eutectic point	Reference
		%	
Sucrose	− 14.5	62.58	10
Dextrose	− 5.3	31.7	7
Levulose	about − 14.5	about 69.0	12

For example, the total sugar content of pressed apple juice is 62.5% levulose, 20% sucrose, and 17.5% dextrose (23). Since apple juice contains a large proportion of levulose, the total sugars solubility curve will closely resemble that of the sucrose-invert sugar-water system although the curve would probably be shifted a little to the right (Figure 4). Because of its higher levulose content, the ice curve of this juice is lower than that of the sucrose-dextrose system with its higher sucrose component. The position of the eutectic point, though not known, probably lies between −23° C. (−9.5° F.) and −25° C. (−13° F.), with a solids concentration of between 67 and 70 g. per 100 g. of solution.

In addition to the above, it should be borne in mind that when sugar solutions contain crystallization inhibitors such as pectins, gums, and other colloidal substances, they can be easily and permanently supersaturated. Therefore lower temperatures than that corresponding to the equilibrium concentration of the eutectic point can be reached during the concentration process, and a higher concentration can be attained. For this reason, the opinion that sugar-containing natural juices cannot be concentrated by freezing to more than 62% solids is not, theoretically, true.

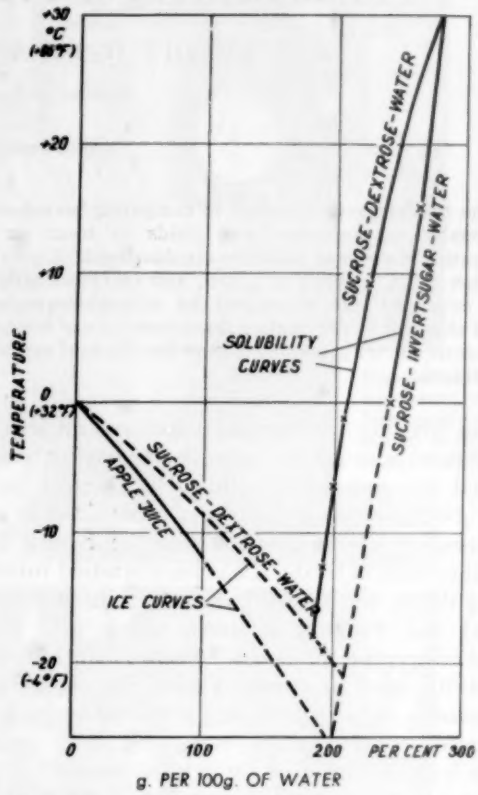


FIG 4. Ice curves and solubility curves, respectively, of sucrose-dextrose-water (11), sucrose-levulose-water (17), sucrose-invert-sugar-water (8), and apple juice.

PRACTICAL PROCESS

In practice the yield is never 100%, since a solution residue will always remain in the capillary spaces and contact angles of the ice. According to the Gibbs and Thomson formula, the amount of dissolved substances (x_1), adsorbed to a unit of surface increases as the surface tension is reduced with increased concentration of (x_2), the solution: $x_1 = -x_2/RT\,(d\sigma/dx_2)_0$, where R is the gas constant, T the absolute temperature, and σ a surface tension. Since malonic, malic, tartaric, and citric acids possess capillary activity, fruit acids may be expected to be concentrated in the ice residue. This concentration actually occurs in practice. On the other hand, ascorbic acid (Vitamin C) is accumulated in the concentrate (Table 2) in accord with the fact that aqueous solutions of ascorbic acid show no capillary activity *(9)*. In experiment II shown in Table 2, 8.67 mg. of fruit acids were found in the ice residue, although without an accumulation caused by capillary activity, only 6.3 mg. could be expected. On the other

TABLE 2

Fruit Acid and Ascorbic Acid in the Ice Residue and in the Concentric from Lemon Juice. ($k = 2.75$, $E = 0.84$)

Sample	Solids, %	Ice residue, concentrate, %	Fruit acids per g. solids, mg. equivalent I	Fruit acids per g. solids, mg. equivalent II	Balance fruit acids mg. II	Ascorbic Acid in 100 g. solids, mg.	Balance ascorbic acid, mg.
Initial juice	7.8	(100.0)	10.5	10.0	39.0	520.5	20.3
Residue	1.8	69.6	12.5	13.78	8.67	136.5	0.86
Concentrate	21.4	30.4	10.28	9.38	30.1	596.5	19.14

hand, only 0.86 mg. of ascorbic acid were found, although, according to the distribution of the solids, 3.27 mg. of ascorbic acid should have been present in the residue.

The supposition that aromatic substances would accumulate in the ice residue did not prove true with an apple juice test. With every process for achieving phase separation in an unclosed system, however, small losses of aromatic substances from both the ice and the concentrate are possible. The flavor preservation with freeze concentration was better than with the extensively used method in which the vacuum concentrate of 53.3% solids is mixed with fresh juice in the proportion of 2.65:1 in order to obtain a concentrate of about 42% solids that is enriched with natural flavor *(4)*. A comparison of the two processes for orange juice and grapefruit juice is shown in Table 3.

TABLE 3

Comparison of the aroma yield (as mg. equivalents potassium dichromate required for the oxidation per g. of dry material) with vacuum process and freeze-concentration.

Concentrate	Total solids %	Aroma yield %
Orange concentrate (vacuum process, 27.3% juice of 12.0% total solids added)	42.15	26.8
Orange concentrate (freezing process)	39.3	About 60.0 (on account of losses by evaporation during centrifuging)
Grapefruit concentrate (vacuum process, 27.8% juice of 12.2% total solids added)	41.15	43.4
Grapefruit concentrate (freezing process)	42.0	79.0

It has been suggested that it is practically satisfactory if the ice residue contains a small amount of solids, say 0.5 or 1%. It may be seen from the following discussion that this generalization is not correct. If ϵ stands for yield, then $\epsilon = 100\ g_f\ x_f / g_s\ x_s$. The solids content of the ice residue is defined in the following manner: $x_R = 100\,(g_s x_s - x_f g_f)/g_s - g_f$ thus, $\epsilon = (1 - x_R/x_s)/(1 - x_R/x_f)$ or $x_R = x_f\,(1 - \epsilon)/(x_f/x_s - \epsilon)$.

In Figure 5, the ratio residue concentration to initial concentration, (x_R/x_s), dependent on the concentration ratio k, is plotted for various yield data, ϵ. A 95% yield, for instance, corresponds to a 0.95% residue concentration for a 10% initial solution that is concentrated to the double concentration $[x_R = (x_R/x_s)\,x_s]$.

If a one and a half-fold concentration is satisfactory, then for the same yield, the residue may contain 1.35% solids. With a three-fold concentration and the same yield, however, only 0.72% solids is allowable in the residue. If the initial solution is more dilute, the solids content of the ice residue must be lower to obtain the same yield. On the other hand, a residue of 2.38% solids is permissible when a 25% initial solution is used to obtain 50% solids in the concentrate. Only on such basis is it possible to judge the value of various practical procedures. Yield data or residue losses are valueless unless the concentration ratios are stated.

To determine the concentration that can be attained in actual practice, one must consider that every concentrating process is connected with a given heat supply. This can be in the form of transmitted heat or in the form of the heat equivalent of the energy requirement for separating the components. This heat supply causes a certain amount of ice to melt, and the actual attainable concentration is therefore lower than the theoretical one. If the theoretical concentration, x_f, (Figure 6) is to be attained, one must choose a freezing temperature (t'_f) so low that the concentration decrease $(x'_f - x_f)$ effected by melting $(G_E - G'_E)$ is

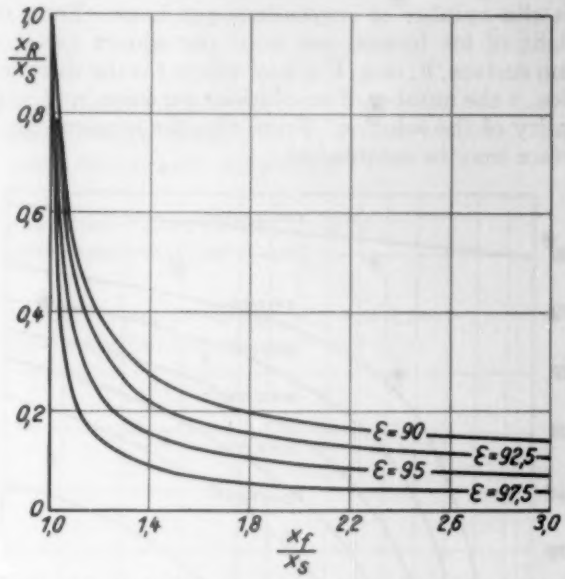


FIG. 5. Ratio of residue concentration to initial concentration (x_R/x_s), dependent on the concentration ratio (x_f/x_s), with various yields.

compensated for. As with falling temperature the slope of the equilibrium curve of the solids decreases (Figure 6, Curve I), the difference between practical and theoretical freezing temperatures $(t'_f - t_f)$ becomes considerably greater with increasing final concentration, even when a constant amount of melting ice $(G_E - G'_E)$, independent of temperature, is assumed. Thus, it can be seen that, for economic

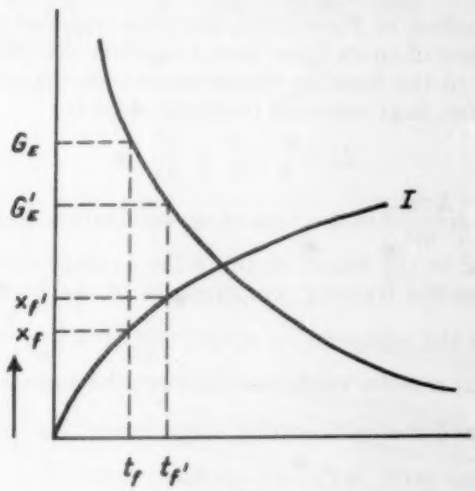


FIG. 6. Connection between the freezing temperatures theoretically and practically necessary for attaining a certain concentration ratio. (See text for explanation.)

reasons, every procedure of freeze-separation has an upper limit for the concentration ratio which must not be exceeded.

The cold requirement for freezing out one liter of fruit juice is shown in Figure 7. For a practical process the temperatures necessary to obtain the desired concentrations must be established. If freezing is carried out continuously on a drum with the surface F, the volume of ice which freezes out per revolution with an average density of the solution γ, is: $v_0 = g/n\gamma$, where g is the weight of water frozen out per hour and

n is the number of revolutions per hour. Thus the weight of ice formed per hour per square meter of drum surface, F, is: $g/F = n\delta\gamma$, where δ is the thickness of ice, n the number of revolutions per hour, and γ the density of the solution. From this the required drum surface may be established.

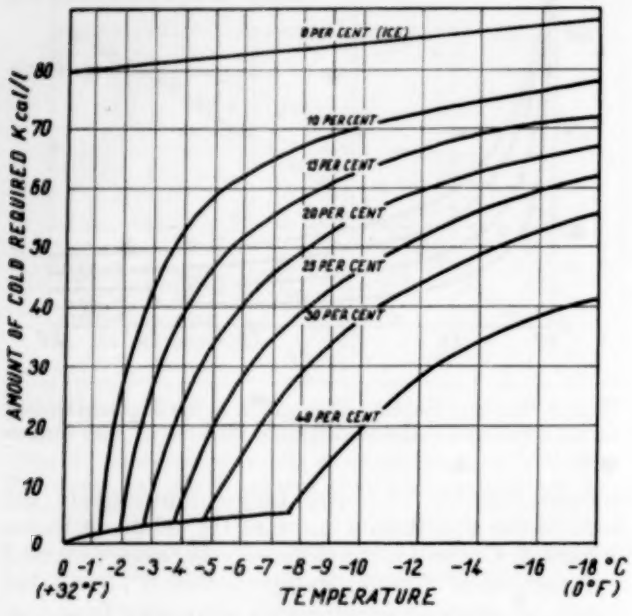


FIG. 7. Cold required for freezing apple juice of various concentrations at different temperatures in order to attain various final concentrations.

According to Plank *(13)*, the time required for the formation of an ice layer from a solution that has been cooled to the freezing temperature (one dimensional heat flow, heat removed from one side) is:

$$Z_0 = \frac{\rho}{\theta}\left(\frac{\delta}{K} + \frac{\delta^2}{2\lambda}\right),$$

where $\rho\left(\frac{\text{kcal.}}{\text{m}^3}\right)$ is the heat of crystallization (referring to 1 m^3 in the frozen state), θ the average difference between the freezing temperatures of the liquid and that of the refrigerating agent; and $K = \left(\frac{\text{kcal}}{\text{h. m}^2\ °\text{C.}}\right)$ the heat transfer coefficient between the surface of the drum and the refrigerating agent inside. As $\frac{\delta Fe}{\lambda Fe} \ll \frac{1}{\alpha}$, one may with sufficient accuracy term K = to the value of α, and $\lambda\left(\frac{\text{kcal.}}{\text{m.°C.h}}\right)$ the thermal conducting coefficient of the ice layer with the thickness, δ. Since the drum dips into the liquid with η times the amount of its circumference, Z_0 is η/n. From the equation for Z_0 we get the relation between the number of the cylinder revolutions and the layer thickness of the ice at given α, θ, λ, ρ, and η,

$$n = \frac{\eta\theta}{\rho\left(\frac{\delta_0}{\alpha} + \frac{\delta_0^2}{2\lambda}\right)}$$

Since in practice the value of δ lies between 2 and 12 mm., it follows that n can be regulated at a ratio of 11 to 1.

By comparing the theoretical and actual cold requirements for obtaining a certain concentration, one may define the efficiency of a concentration procedure. The efficiency, along with the yield, ϵ, characterizes the utility of the process. The efficiency is determined by the specific energy supply, while the yield is dependent on capillary and surface tension as shown below.

CRYSTAL STRUCTURE

In the freezing process, pure ice separates out in larger or smaller crystals according to temperature conditions. The concentrate is located on the surface layer of these crystals or in the intermediate spaces. As a working hypothesis, the same conditions as exist in cylindrical capillaries are assumed.

The capillary rise, h, is indicated by the well known equation: $h = 2\sigma/r\gamma g$, where σ is the surface tension of the solution, γ the density, r the capillary radius, and g the acceleration.

The smallest residue (R), remaining in the capillaries is found by the formula $R = r^2\pi h = 2r\pi\sigma/\gamma g$, and depends mainly on the capillary radius and the acceleration since the surface tension and density of fruit juices do not vary much. From these theoretically determined residues, a method was developed at our institute by Görling *(5)* for the determination of the capillary distribution curves of frozen juice samples (Figure 8).

The velocity of reaching this final state is indicated by the speed, c_r, with which a certain volume of solution, V_r, runs from a capillary with the radius r. Thus, $c_r = dV_r/dt$.

The increasing amount of juice that drops from a sieve-like closed pipe, filled with ice slush, can be regarded as the summation of all of the V_r's of the capillaries existing in the slush (Figure 9). According to the Hagen-Poiseuille equation: $dV/dt = \pi\Sigma r^4\Delta P/8\eta l$, where V is the volume of drained juice, t the time in seconds, r the capillary radius in meters, η the dynamic viscosity in centipoises, l the height of the ice pillar in meters, and ΔP the pressure difference between the upper and lower ends of the capillary in kg. per $m.^2$. It is possible from this equation to calculate an average capillary radius. The radius depends on the draining time, since only the filled capillaries affect the draining velocity and the wide capillaries are emptied first. The results (Table 4) agree with the much more refined measurements of Görling (Figure 8).

The dynamic viscosity, as well as the other factors mentioned, plays decisive role in the Poiseuille equation. Since only the viscosities of sucrose solutions are available in the literature, the viscosity of black currant juice was determined experimentally. The

TABLE 4

Test	Initial concentration, %	Freezing Temperature, °C.	Freezing rate	Storage time and temperature	Test temperature, °C.	Size of the capillary radii, mm.
1	12.4	− 10	quick	No storage	− 3.6	0.16–0.11
2	12.4	− 10	quick	14 days at − 4.0°C.	− 4.0	0.45–0.19
3	12.4	− 10	slow	24 hours at − 3.0°C.	− 4.0	0.53–0.16
4	12 4	− 10	quick	14 days at − 4.0°C.	− 4.4	0.65–0.17
5	35.0	− 13	quick	No storage	− 13.0	0.85–0.22

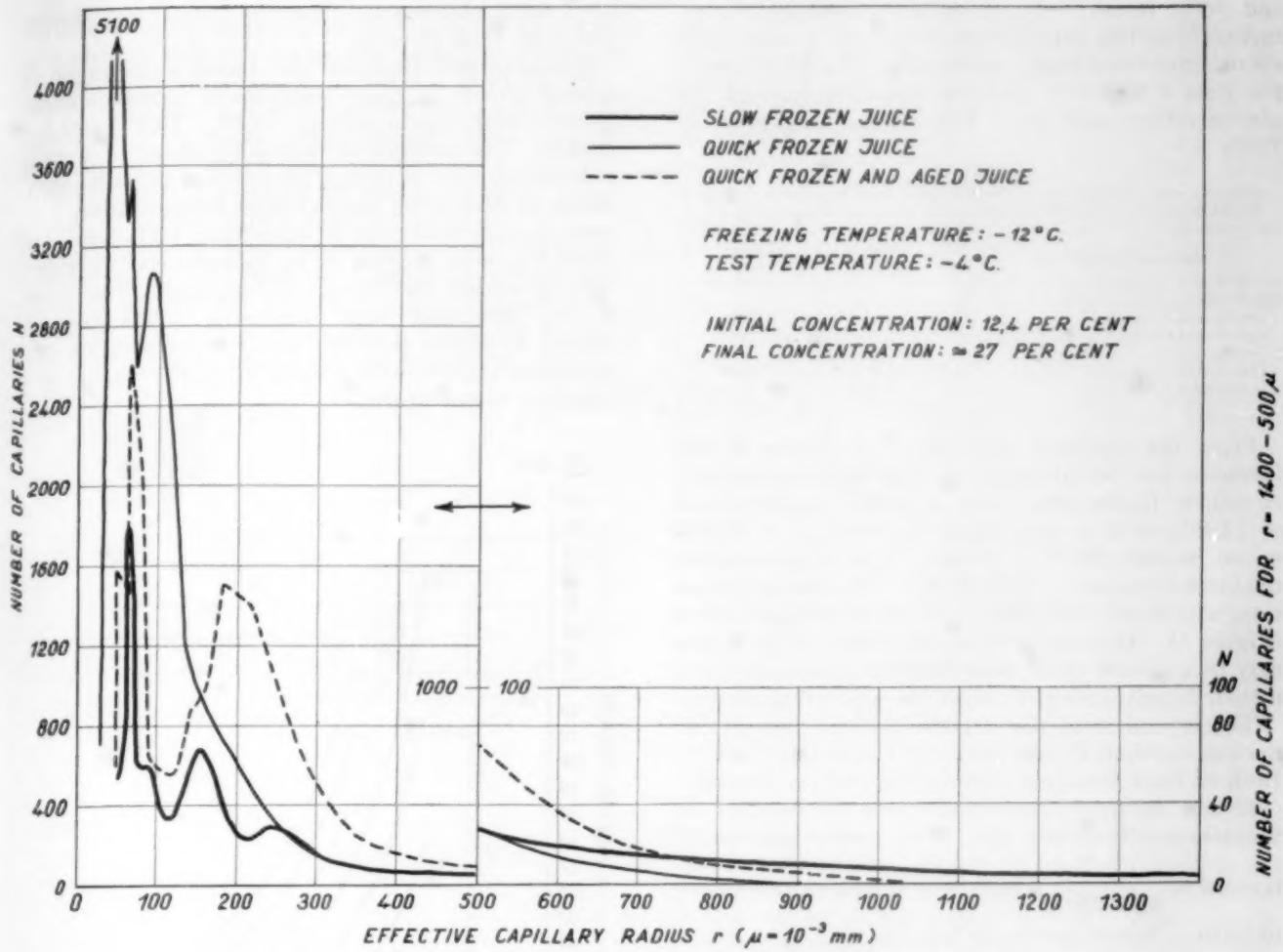

5100
SLOW FROZEN JUICE
QUICK FROZEN JUICE
QUICK FROZEN AND AGED JUICE
FREEZING TEMPERATURE: −12°C.
TEST TEMPERATURE: −4°C.
INITIAL CONCENTRATION: 12,4 PER CENT
FINAL CONCENTRATION: ≈ 27 PER CENT
NUMBER OF CAPILLARIES N
NUMBER OF CAPILLARIES FOR r = 1400 − 500 μ
EFFECTIVE CAPILLARY RADIUS r (μ = 10⁻³ mm)

FIG. 8. Capillary distribution curve and number of capillaries with various radii.

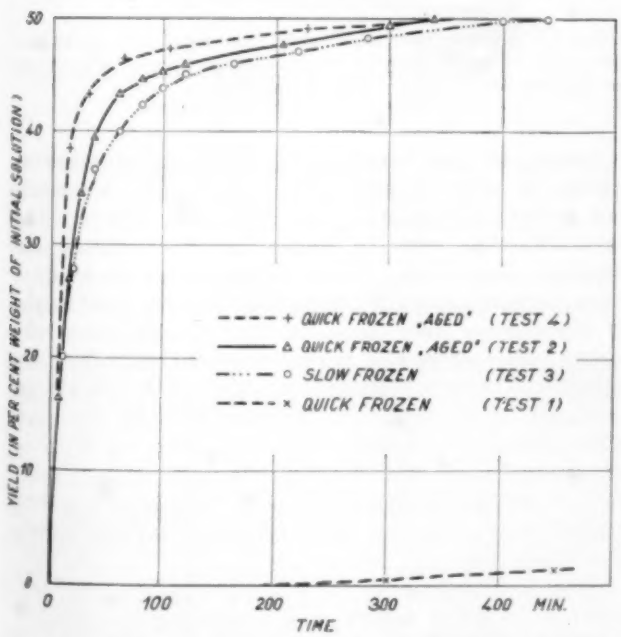

+ QUICK FROZEN „AGED" (TEST 4)
△ QUICK FROZEN „AGED" (TEST 2)
○ SLOW FROZEN (TEST 3)
× QUICK FROZEN (TEST 1)
YIELD (IN PER CENT WEIGHT OF INITIAL SOLUTION)
TIME
MIN.

FIG. 9. Yield of concentrate flowing from a tube filled with ice squash. All experimental results were calculated for a temperature of −3.6° C., theoretical yield 50%.

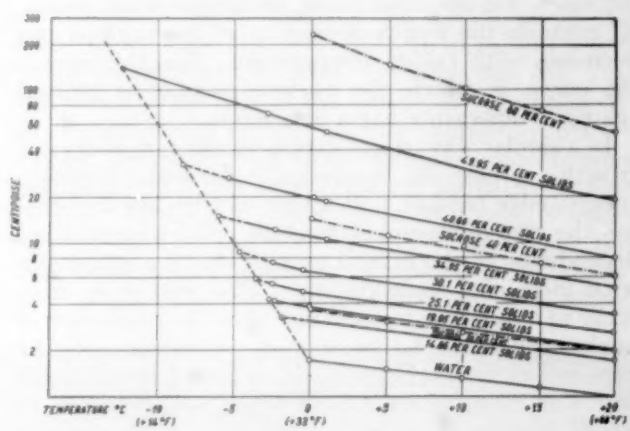


FIG. 10. Effect of temperature on the viscosity of black currant juice and sucrose solutions.

concentration and temperature were varied (Figure 10). Both Figure 8 and Table 4 show that the capillary radii depend on freezing conditions, and that in prolonged storage the number of capillaries with larger capillary diameter increases. The initial concentrations of black currant juice, frozen at two extreme rates of refrigeration necessary for yields of 95

and 90%, respectively, were determined by centrifuging. For this experiment, the speed, n, was 3,000 r.p.m., the centrifugal acceleration 11,000 m./sec.^{2}, the time 2.5 and 15 minutes, respectively, and the concentration ratio 2:1. The results are shown in Table 5.

TABLE 5

Highest Initial Concentrations of Black Currant Juice Required in Order to Obtain 90 and 95% Yield, Respectively, with a Concentration Ratio of 2:1.

Method of preparation	Yield 95%	Yield 90%
Quickly frozen		
centrifuged 2.5 min.	4.8	11.5
centrifuged 15 min.	7.3	15.5
Slowly frozen		
centrifuged 2.5 min.	12.4	28.0
centrifuged 2.5 min.	17.0	—

From the capillary radii shown in Figure 8, the following can be calculated for the final equilibrium: A quickly frozen juice, with an initial concentration of 12.4%, with a centrifugal acceleration of 11,000 m./sec.^{2} yields 96.7%. A slowly frozen juice, under the same conditions, yields 97.5%. The concentration ratio was nearly the same as in previous experiments (Figure 8). The vital importance of crystal structure may be gathered from these considerations, especially if there is only a short time for the separating process.

The crystal structure depends on the ratio of the nucleus number, Z, and the rate of crystal growth, v. Both of these concepts were introduced by Tamman *(18)* and deduced theoretically and statistically by Stranski and Kaischew *(16)*. The nucleus number, Z, is equal to $\frac{K}{e^{-\frac{F\sigma}{3RT}}}$ where $\frac{F\sigma}{3}$ is the energy necessary to form a three-dimensional nucleus with the surface, F, and the interface tension against the liquid phase, σ. Since this energy decreases with falling temperature, T, the nuclei become smaller with increased undercooling (supercooling), while the number of nuclei increases. On the other hand, the proportional factor, K, contains the length of edge, a, of the nucleus and decreases with falling temperature. For this reason the curve in which the nucleus number is plotted against temperature has a maximum.

In a similar way, the equation for the rate of crystal growth, v, may be theoretically derived. Forming energy, edge tension, and length of edge are included for the two-dimensional nucleus. The temperature dependency of the crystal growth shows a maximum with increasing undercooling. This maximum may occur at a different temperature than the maximum of nucleus number. Large crystals, therefore, may be expected in temperature ranges where Z is still small and v is large, whereas with lower temperatures, at which Z has increased considerably, a fine crystal structure arises. Besides the factors included in the equations, these curves are influenced by external circumstances, such as viscosity of solution (and with it a change of diffusion rate), heat-transfer conditions, and adsorption on the crystal surface. Thus, the v of aqueous dextrose or levulose solutions is considerably higher than the v of sucrose or lactose solutions of the same concentrations *(1)*. That the maximum of crystal growth was actually in accord with the theoretical calculations was shown by Volmer and Marder *(22)* with pure glycerol.

Tamman and Büchner *(20)* found a maximum of crystal growth in sugar solutions of various concentrations with approximately −12°C. (10.5°F.) undercooling. The addition of increasing amounts of sugar reduces the rates of crystal growth and shifts the maximum to decreasing undercooling temperatures. Our own measurements are in agreement with this. The crystal growth proved to be proportional to undercooling within the range investigated. The slope, dv/dt, decreased with increasing solids content. Figure 11 shows that the linear crystallization rate decreases rapidly with increasing concentration at a constant temperature.

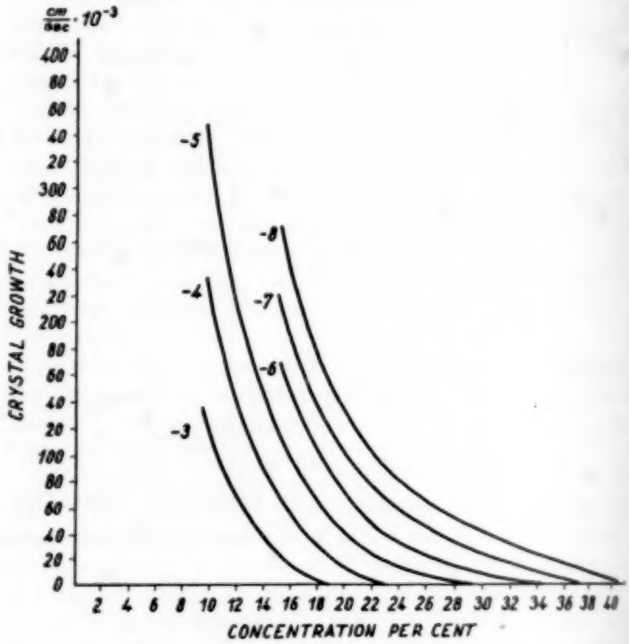


FIG. 11. The linear crystallization rate, depending on the concentration of apple juice for various temperatures. The curves are plotted for a concentration ration 2:1.

Owing to the rapid increase of the number of nuclei, Z, with considerable undercooling, we could not achieve a maximum rate of crystal growth. The crystallization velocity shows its effect during the freezing on drums. When factors such as kind of juice, temperature difference, heat transfer, and height of dipping are held constant, the concentration, viscosity, and content of turbid material, all affect the number of drum revolutions required to obtain an ice-layer of a certain thickness. This means that, when using the "number of revolutions vs. layer of thickness" curve, the revolution number chosen must be low enough so that the crystallization rate will be sufficient to form the desired layer thickness within the given time.

The nucleus number, Z, was measured by Rau *(14)* with pure water which was condensed on polished metal surfaces in a vacuum. He found the maximum at −11°C. (12°F.), and a lower pre-maximum at −4°C. (25°F). Our own experiments with sugar-

containing juices, according to the method of Tamman *(21)*, showed that the metastable phase, in which no spontaneous crystallization is possible, is about 5°C. (9°F.) below the freezing point of the solution. Z rises steeply at lower temperatures. Here, too, a maximum could not be achieved because of spontaneous crystallization caused by the particularly great number of crystallization-inducing particles.

With increasing initial concentration, and the same concentration ratio, both the number of centers and the rate of crystal growth increase (Figure 10). Therefore, concentrated solutions must be frozen more slowly than more dilute ones in order to obtain

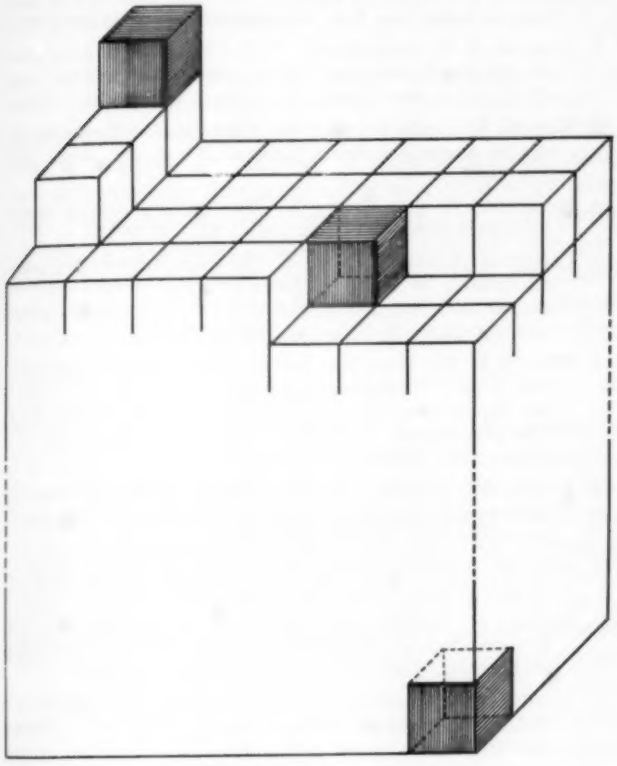


FIG. 12. Scheme of a crystal-cube.

sufficiently large capillary radii. This is confirmed in Table 5, where the yield of concentrate is shown to be high only when the black currant juice is frozen slowly.

As shown in Figures 8 and 9 and Tables 4 and 5, storage has a great influence on the size of crystal spaces and hence on yield. This is caused by recrystallization. It follows from the Stranski-Kaischew equation that edge length, a, of the arising nucleus corresponds to a certain extent of undercooling and supersaturation. As the scheme of a crystal cube shows in Figure 12, a newly added block in the middle of a plane is held by three neighboring blocks; in an edge-row only two hold it; while the first block of a new level is held by only one neighboring block.

As small crystals have a relatively larger number of edge and corner blocks, the average separation energy for one net level is smaller than with large crystals. Thus, their solubility is greater, and they may dissolve when stored, while the larger crystals continue to grow. We can also explain the greater solubility of smaller crystals by the thermodynamic equation of Thomson and Gibbs: $\ln P_a/P_\infty = 4M\sigma/RTa\gamma$, where P_a is the vapor pressure of a small crystal with edge length a; P_∞ the vapor pressure of a theoretically infinitely large crystal, M the molecular weight, σ the surface tension or interface tension respectively, and γ the density. Using this equation, Weickmann *(24)* calculated the radius of the formed nucleus for a given undercooling and found for pure water that undercooling of −0.02, −4.0, and −10.0°C. (31.5, 25, and 14°F.) was corresponding to radii of 1×10^{-4}, 5×10^{-7}, and 2×10^{-7} cm., respectively.

By means of microphotographs, taken with a Leitz-Panphot camera in a freezing room, we succeeded in making visible the recrystallization of a 12.5% currant juice. Figure 13a shows a growing ice crystal (×3). Figure 13b shows a section of 13a, the central rib of an ice feather (×120). The rate of crystal growth was 8 cm. per hour at −3°C. (26.5°F.). The formation of the ice feather can be explained by the fact that a slight supersaturation of sugar is caused as pure water crystallizes out at the edge of the main crystallization direction. As the heavier solution sinks, slight undercooling occurs along the edge. At a certain degree it suddenly stops, and a new crystal forms with the same crystallization rate *(2)*. The notch at the root of the side crystal is caused by the higher initial crystal growth caused by undercooling. Increasing the initial solution concentration and the freezing rate encourages the formation of side crystals. Figure 13c shows the same section 5 hours later at −3°C. (26.5°F.). It can be seen that the large crystals have grown at the expense of the smaller ones. Figure 13d shows a quickly-frozen juice where

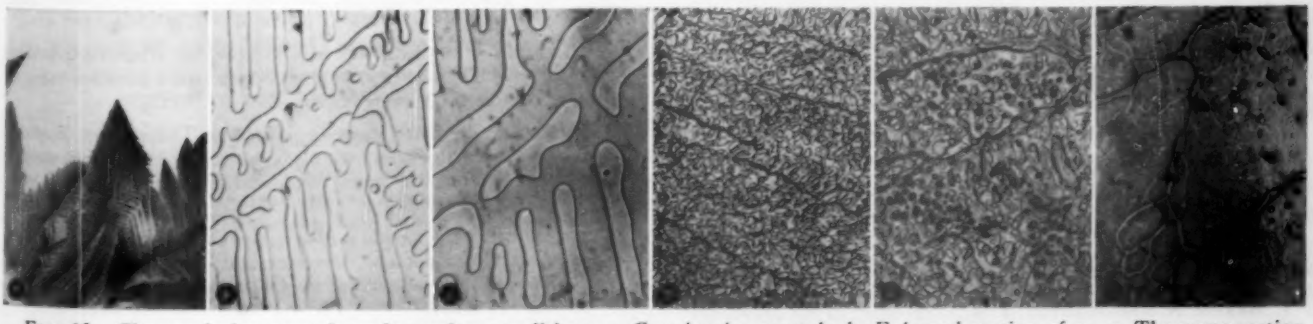


FIG. 13. Changes in ice crystals under various conditions. a. Growing ice crystal. b. Enlarged section of a. c. The same section of an ice crystal of b, 5 hours later. d. Crystal structure of a quickly frozen juice. e. Crystal structure of a quickly frozen juice after storage at −13° C. for 20 hours. f. Crystal structure of a quickly frozen juice after storage at −6° C. for 20 hours.

the crystal growth was several cm. per sec. at −13°C. (8.5°F.). Figure 13e shows the same juice after 20 hours at the same temperature. The crystal structure has become slightly coarser. In Figure 13f a juice quickly frozen at −13°C. (8.5°F.) is shown after 20 hours of storage at −6°C. (21°F.). Large ice sheets have formed, and the previous course of the ice feather is no longer discernible. The entire crystal surface has been considerably diminished.

While recrystallization in supersaturated solutions and melts can thus be explained, Tamman *(19)* offers another explanation of recrystallization in solids. He states that as there are differences of energy at the contact points of differently oriented crystals, they will try to orient themselves. This can be affected by the mobility of the atoms in the crystal gratings at sufficiently high temperatures. Crystallographically congruent planes may grow together, especially under pressure. The Linde-Krause Patent No. 669,185 DRP is based on this process.

SUMMARY

As a basis for concentrating fruit juices, the dependency of the freezing point on concentration is determined and the location of the eutectic point is taken into consideration. The theoretical yield can be calculated by means of the ice curve.

In practice, however, some concentrate residue always remains in the capillary spaces and in the angles of contact. Therefore, depending on the separation method applied, the actual yield is more or less below the theoretically computed yield. Substances which reduce the free energy of the surface by reducing the surface tension, will diffuse from the interior of the liquid enclosed in the capillaries towards the surface. Therefore, they are concentrated within the ice surface. On the other hand, substances which will not reduce the surface tension will accumulate in the concentrate. The relationships between yield data, concentration ratio, and solids in the ice residue are discussed. The concentrate residue remaining in the ice is dependent on the crystal structure which is characterized by the capillary distribution curve. This, in turn, depends on the relationship between the crystal growth, and the nucleation. The crystal size is, furthermore, changed by recrystallization. This relationship, shown by the capillary distribution curve, is also demonstrated by microphotographs.

Since every concentration process is connected with an energy supply which causes ice to melt, the concentration actually attainable by freezing differs from the theoretical. The ratio between the theoretical and practical amount of cold required to obtain a certain concentration is called the efficiency coefficient of the concentration procedure. The higher the desired concentration, the less efficient the procedure becomes.

LITERATURE CITED

1. Braun, A. and Walton, J. A. The effect of dissolved substances on the velocity of crystallization of water. *J. Am. Chem. Soc.*, **38**, 320 (1916); **40**, 1178 (1918).
2. Breitner, H. J. Rhythmische Kristallisation beim Gefrieren von Wasser. *Kolloid-Z.*, **111**, 81 (1948).
3. McCready, R. M., Walter, E. D. and Maclay, W. D. Sugars of citrus juices. *Food Technol.*, **4**, 29 (1950).
4. Florida Canners Cooperation. Frozen concentrated citrus juice. *Food Inds.*, **21**, 906, 930 (1949).
5. Görling, P. Physikalische Vorgänge bei der Entwässerung von Lebensmitteln durch Schleudern. *Z. Ver. deut. Ing.*, **91**, 110 (1947); see also: Krischer, O., Grundgesetze der Feuchtigkeitsbewegung in Trockengütern. *Z. Ver. deut. Ing.*, **82**, 373 (1938).
6. Heiss, R., Untersuchungen über den Kältebedarf und die ausgefrorenen Wassermengen beim schnellen und langsamen Gefrieren von Lebensmitteln. *Z. ges. Kälte-Ind.*, **40**, 53 (1933).
7. Jackson, R. F. and Silsbee, C. G. The solubility of dextrose in water. *Nat. Bur. Standards, Sci. Papers*, 437 (1922).
8. Jackson, R. F., and Silsbee, C. G. Relations of saturation of systems containing sucrose, dextrose, levulose and water. *Nat. Bur. Standards, Technol. Papers*, 259 (1924).
9. Keller, C. J. and Künzel, O., Über die Oberflächenaktivität der wasserlöslichen Vitamine. *Z. ges. exp. Med.*, **103**, 704 (1938).
10. Kremann, R. and Eitel, H. The ternery system sugar-citric acid-water. *Rec. trav. chim.*, **42**, 539 (1923).
11. Leighton, A. and Leviton, A. The solubility-freezing point relationship of water solutions saturated with respect to sucrose and dextrose in relation to the storage of sherbet and water ice. *J. Dairy Sci.*, **18**, 801 (1935).
12. Loomis, E. H., Über den Gefrierpunkt wässriger Lösungen von Nichtelektrolyten. *Z. f. physik. Chem.*, **37**, 414 (1901); see also Jackson, R. F., Silsbee, C. G., and Profit, M. J. The preparation of levulose. *Nat. Bur. Standards, Sci. Papers*, 519 (1926).
13. Plank, R., Beiträge zur Berechnung und Bewertung der Gefriergeschwindigkeit von Lebensmitteln. *Beihefte zur Z. ges. Kälte-Ind.*, Serie **3**, (10) (1941).
14. Rau, W. Gefriervorgänge des Wassers bei tiefen Temperaturen. *Schriften Deut. Akad. Luftfahrtforsch.*, **8**, (2) (1944).
15. Riedel, L. Brechungsvermögen und Gefriertemperatur von Fruchtsäften in Abhängigkeit von der Konzentration. *Z. Lebensm. Untersuch. u. Forsch.*, **89**, 289 (1949).
16. Stranski, J. N. and Kaischew, R., Kristallwachstum und Kristallkeimbildung. *Physik. Z.*, **36**, 393 (1935). (Extensive literature).
17. Taketomi, N., Kumagaja, T. and Kikuraku, R. Effects of impurities on the solubility of sucrose. *J. Soc. Chem. Ind., Japan* (suppl.), **34**, 190B (1931).
18. Tamman, G. Kristallisieren und Schmelzen. 1903. Verlag Barth, Leipzig.
19. Tamman, G. Zur Deutung der Rekristallisation. *Z. anorg. Chem.*, **113**, 163 (1920).
20. Tamman, G. and Büchner, A. Die Unterkühlungsfähigkeit des Wassers und die lineare Kristallizationsgeschwindigkeit des Eises in wässrigen Lösungen. *Z. anorg. Chem.*, **222**, 371 (1935).
21. Tamman, G. and Elsner V. Gronow, H. Über die spontane Kristallization unterkühlter Schmelzen und übersättigter Lösungen. *Z. anorg. Chem.*, **200**, 57 (1932).
22. Volmer, M. and Marder, M. Zur Theorie der linearen Kristallisationsgeschwindigkeit unterkühlter Schmelzen und unterkühlter fester Modifikationen. *Z. physik. Chemie*, A, **154**, 97 (1936).
23. Warcollier, C. and le Moal, A. Variationen der relativen Anteile von Sucrose, Dextrose und Levulose in Apfelsäften während der alkoholischen Gärung. *Ann. fals. et fraudes*, **28**, 517 (1939).
24. Weickmann, H. Die Eisphase in der Atmosphäre. *Berichte des Deutschen Wetterdienstes in der US-Zone*, No. 6 (1949).

Comparison of Scoring Results for Two and Four Samples of Corn Per Taste Session

ALICE COLLINGS WARD AND MILDRED M. BOGGS
Western Regional Research Laboratory,[a] Albany, Calif.

(Manuscript received March 5, 1951)

Four samples of frozen corn that differed only slightly in flavor were scored with two and also with all four samples in single taste sessions. Judges did not consistently show better performance with two than with four samples.

The purpose of the work reported here was to compare judges' performance when they scored 2 and 4 samples of frozen corn per taste session. A large number of samples per session is economical but many workers consider that accuracy is sacrificed when more than two are scored concurrently. In measuring judges' performance, two factors require attention: ability to detect differences between samples, and ability to repeat the detection of differences on repeated tastings. This experiment was planned to test these factors.

LITERATURE

The largest number of samples scored in one session for which there is evidence of satisfactory performance was reported by Sharp, Stewart, and Huttar *(7)*. One hundred and sixty egg samples were scored within two hours. Bengtsson and Helm *(1)* in referring to tests in which 100 or more samples of butter were scored in one period, say that "with such a high number it is inconceivable that small differences in flavor can be detected. This practice cannot, therefore, he recommended for experimental work." McCammon, Pittman, and Wilhelm *(5)* found results unreliable when flavor of more than 10 or 15 egg samples were scored at one time. Some investigators *(1, 2, 4, 6)* usually limit the number to only 2 or 3 samples. The writers seldom use more than 4 samples when flavor is the factor under consideration but have satisfactorily used up to 12 samples for color or texture. Hopkins *(4)* reported on the influence of 2, 4, and 8 samples containing varying amounts of additives. He found that varying the number of samples significantly affected the relation of average score to composition in only one instance. In this case the subjects were more sensitive to differences in intensity of additive when samples were submitted in sets of 4 or 8 than when they were submitted in pairs.

EXPERIMENTAL

Samples were purposely selected that differed only slightly in flavor in order to compare the two appraisal procedures under difficult conditions. The samples were frozen corn that had been held in the husk at 0.5° C. (33° F.) for 0, 2, 3, and 4 days prior to processing. Processing consisted of the usual commercial procedures.[b] The unthawed corn was cooked for 8 minutes in a steamer.

Scoring Procedure. One of the following sets of samples was scored at each taste session: (a) corn held for 0, 2, 3, and 4 days prior to processing, (b) 0 and 2, (c) 0 and 3, (d) 0 and 4, (e) 2 and 3, (f) 2 and 4, and (g) 3 and 4 days. The four-samples-per-session test was replicated 6 times and each of the pairs twice, giving 6 replications per sample when pairs were combined into complete blocks.

The panel consisted of 8 trained, selected tasters. It was well prepared for this study, having scored similar corn samples daily for 2 months just prior to the present series. A score of 5 indicated pronounced natural, sweet flavor and a score of 1, weak corn flavor and little sweetness.

RESULTS AND DISCUSSION

The analysis-of-variance summary table and the mean scores for each sample by the two methods are reported in Table 1.[c]

TABLE 1

Analysis of Variance

	Two samples per session		Four samples per session	
	Degrees of freedom	Mean squares	Degrees of freedom	Mean squares
Treatments	3	7.50 [b]	3	6.87 [b]
Judges	7	3.02 [b]	7	2.99 [b]
Blocks	2	0.27	....	.....
Interactions				
Treatments x judges	21	0.56	21	0.52
Treatments x blocks	6	0.36	....	.....
Judges x blocks	14	0.48	....	.....
Treatments x judges x blocks	42	0.50	....	.....
Error	96	0.50	148	0.62
Total	191	.....	179	.....
Average scores 0 days of storage	3.76		3.51	
Average scores 2 days of storage	3.56		3.40	
Average scores 3 days of storage	3.32		3.14	
Average scores 4 days of storage	2.84		2.63	
Least significant difference, 1% level	0.38		0.43	

[b] Significant at 1% level.

The trends for score decreases with storage time are similar by the two taste methods. The per-unit mean squares for treatments, 0.15 and 0.16, are very close, indicating no important treatment differences from method to method. The F ratio for reproducibility based on pooled errors for treatments, 0.61/0.51 = 1.20, is not significant even at the 5% level, indicating

[a] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[b] The authors wish to acknowledge the cooperation of L. H. Pollard, Utah Agricultural Experiment Station, for supplying the corn and of F. E. Lindquist of this Laboratory for processing it.

[c] The authors wish to acknowledge the help of S. B. Clark, Bureau of Agricultural Economics, with the statistical analysis and interpretation of the data.

no important difference in reproducibility of the two methods. Thus, judges' performance does not appear to differ whether 2 or 4 samples are scored concurrently, and the more efficient four-a-day design would be the preferred method for corn. It is recognized that different results might be obtained with other commodities, especially strongly flavored foods or those with textures such that their flavor cannot be removed from the mouth easily.

It is of interest that blocks have no significant effect on scores since Hanson, Kline, and Lineweaver *(3)* found that quality of samples submitted together had a marked effect on scores for a given sample. They found that a given sample was scored high in the presence of poor samples and low in the presence of good samples. The bland flavor of corn or the small variation in quality of samples in the present experiment may account for the uniformity of scores in the different blocks.

LITERATURE CITED

1. Bengtsson, K., and Helm, E. Principles of taste testing. *Wallerstein Lab. Commun.*, **9**, 171 (1946).
2. Dove, W. F. Technics for measuring changes in flavor acceptability. Committee on Food Research, Conference on deterioration of fats and oils. QMC Manual 17-7, 84 (1945).
3. Hanson, Helen L., Kline, Leo, and Lineweaver, H. Application of balanced incomplete block design to scoring of ten dried egg samples. *Food Technol.*, **5**, 9 (1951).
4. Hopkins, J. W. A procedure for quantifying subjective appraisals of odor, flavor and texture of foodstuffs. *Biometrics Bull.*, **6**, 1 (1950).
5. McCammon, R. B., Pittman, M. S., and Wilhelm, L. A. The odor and flavor of eggs. *Poultry Sci.*, **13**, 95 (1934).
6. Moser, H. A., Jaeger, C. M., Cowan, J. C., and Dutton, H. J. The flavor problem of soybean oil. II. Organoleptic evaluation. *J. Am. Oil Chemists Soc.*, **24**, 291 (1947).
7. Sharp, P. F., Stewart, G. F., and Huttar, J. C. Effect of packing materials on the flavor of storage eggs. New York Agr. Expt. Sta., Ithaca Memoir, **189** (1936).

An Improved Manometric Technique for Evaluating the Oxidative Stability of Coldpressed Orange Oil

J. W. KESTERSON and R. HENDRICKSON
Florida Citrus Experiment Station, Lake Alfred, Florida

(Manuscript received January 17, 1951)

An improved manometric technique has been developed by which the true oxygen uptake of coldpressed orange oil can be determined. By this method the carbon dioxide and water evolved by the oil is removed so more realistic stability values can be expected.

Orange oil in general is subject to oxidative changes which may be accelerated by heat, moisture, or catalysts. Off-flavors may develop from products formed during oxidation which are like oxidized turpentine in character and referred to as "terpeney" by the essential oil trade. Since flavor is a criterion of quality, the more stable an oil is toward oxidative off-flavors the more desirable it is.

Various procedures for the determination of off-flavors in orange oil have been developed, most of which are not quantitative. These tests have been organoleptic in nature and for the most part denote the deterioration in flavor and aroma that has already occurred due to atmospheric oxidation. By the use of manometric techniques, which determine the amount of oxygen required to give terpeney odors, relative stability values for fresh orange oil may be established. Such criteria permit the selection of an oil for a particular use.

Previous studies by Proctor and Kenyon *(2)* and by Kesterson and McDuff *(1)* were concerned with attempts to assign relative stability values by measurement of oxygen uptake. The techniques used in those studies have since been found to give erroneous values in some cases because the evolution of carbon dioxide and water vapor interfered with the measurement of oxygen absorbed. This paper describes an improved manometric technique for measuring true oxygen uptake by which more realistic stability values are obtained.

EXPERIMENTAL

Manometric methods for estimating exchange of gases have been used for many years. The type of instrument which has been used most, and the type used in this study, is the Warburg respirometer. The primary principle involved is that, if the temperature and volume of a gas are held constant, changes in the quantity of gas can be measured by difference in pressure, and thus oxygen uptake can be measured.

The improved technique used for evaluating the oils, employing the Warburg respirometer, is as follows: Prior to being put through the procedure the oil sample is dried with anhydrous sodium sulfate. A 1-g. sample of oil is then placed in a 17.5 ml. cell (Aminco 5-202), flushed with dry U. S. P. oxygen for a period of 15 minutes, and then immersed in a constant temperature water bath at 40° C ± 0.3° C. (104° F.). The cell is allowed to reach equilibrium conditions before the run is started and is then shaken at the rate of 80 cycles per minute for the entire run. One ml. of Ascarite is placed in the side arm of the cell to remove the carbon dioxide and water vapor that are evolved. Throughout the entire experiment the respirometer is operated at constant volume and the drop in pressure caused by the uptake of oxygen is read, when possible, at intervals of one hour in order to follow the oxygen consumption. Comparison of stability is made by considering the time required for each sample to take up 1200 microliters (1.2 ml.) of oxygen. At this point the samples are terpeney in aroma and lighter in color. The results obtained are shown in Figures 1-5.

DISCUSSION

In the early uses of the method it was not recognized that essential oils liberated gas and thus no provision was incorporated for removing the evolved gases. In the method described above the improved procedure makes

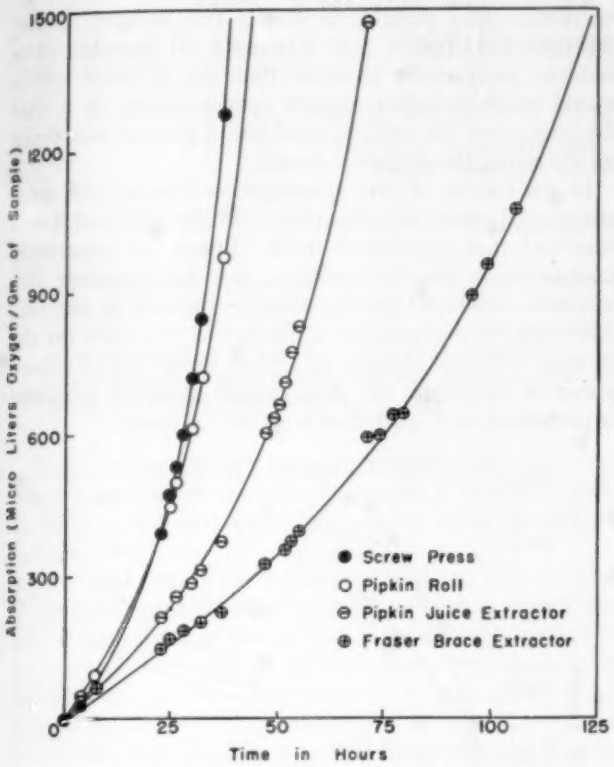


FIG. 1. Microliters of oxygen uptake of Florida coldpressed Valencia orange oil exposed to an atmosphere of oxygen at 40° C. (104° F.).

use of Ascarite to remove these evolved gases. The experiments which led to the development of the improved method are discussed in the paragraphs that follow.

The oils used in these experiments were freshly expressed good quality Valencia orange oils comprising samples of Florida coldpressed oil extracted by four different commercial processes and California coldpressed oil extracted by two different commercial processes. These oil samples were placed in the respirometer as stated above. After 5 hours, the cells containing samples of Florida oils made by the Pipkin roll and by the screw press showed negative pressure, while those samples of oil made by the Pipkin juice extractor (Food Machinery Rotary juice extractor) and Fraser-Brace extractor showed positive pressure. Since the oil was supposed to absorb oxygen it was not expected that positive pressure readings would be encountered, so the experiment was twice repeated, with the same results. It was surmised that the latter two oils must have been undergoing some chemical change from which gas was liberated. It appeared very likely that all four oils were liberating gas but that the first two were absorbing oxygen faster than the gas was being evolved. To substantiate this idea the oils were studied under an inert atmosphere of nitrogen using a modified Dixon-Keilin flask. By the use of specific absorbents the gas evolved was found to be carbon dioxide and water vapor. The amount of evolved gas was measured and the quantities are shown in Figure 3.

Since it was evident that there were at least two reactions taking place simultaneously, one in which gas was evolved and the other in which oxygen was absorbed, it was then obvious that the two oil samples which were more stable liberated gas at a faster rate than they absorbed oxygen and therefore showed initial positive pressure readings. To overcome this effect of evolved gas 1 ml. of a sodium hydrate asbestos absorbent, Ascarite, was placed in the side arm of the cell to absorb the carbon dioxide and water vapor liberated, by which means a true oxygen uptake was obtained. True oxygen uptake rates obtained by the revised procedure are presented graphically in Figures 1 and 2.

Figure 4 shows that the California oils evolved gas as did the Florida oils. Even though both of these oils underwent chemical changes when exposed to an atmosphere of nitrogen, there was no detectable change in the aroma or color of the samples.

Proctor and Kenyon *(2)* in their study of California oils apparently did not encounter positive pressure readings which would indicate that the quality of the oil

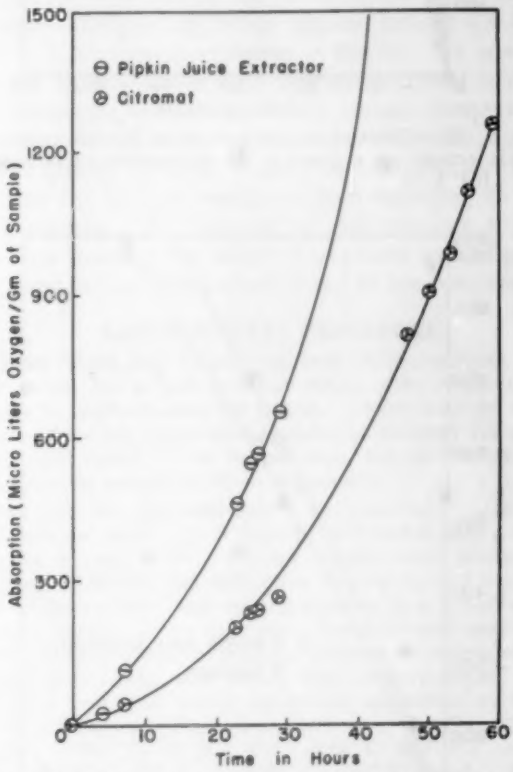


FIG. 2. Microliters of oxygen uptake of California coldpressed Valencia orange oil exposed to an atmosphere of oxygen at 40° C. (104° F.).

used was probably similar to that obtained from the screw press and Pipkin roll. In other words, the oils which they studied apparently absorbed oxygen faster than gas was evolved, and they apparently did not observe the evolution of gas. If this was the case, their values for oxygen absorption would necessarily be low since they were measuring the quantity of oxygen absorbed and the quantity of gas evolved simultaneously. The same comment could be made for the earlier publication by Kesterson and McDuff *(1)*.

Proctor and Kenyon *(2)* also state that, "the deteriorative change in orange oil can be brought about by

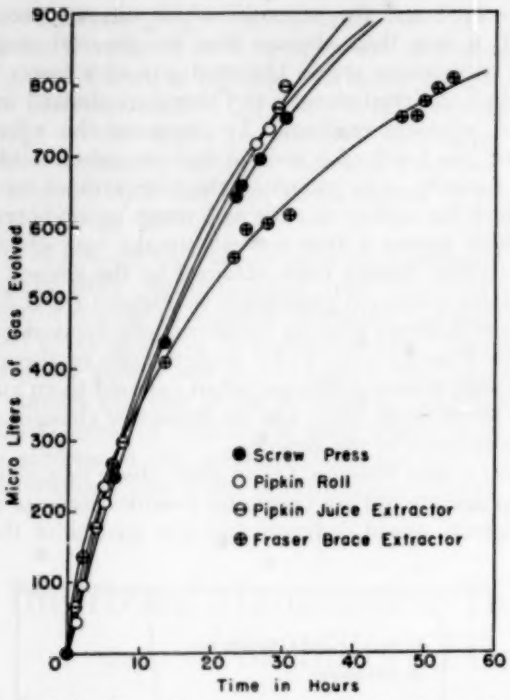


FIG. 3. Microliters of gas evolved from Florida coldpressed Valencia orange oil exposed to an atmosphere of nitrogen at 40° C. (104° F.).

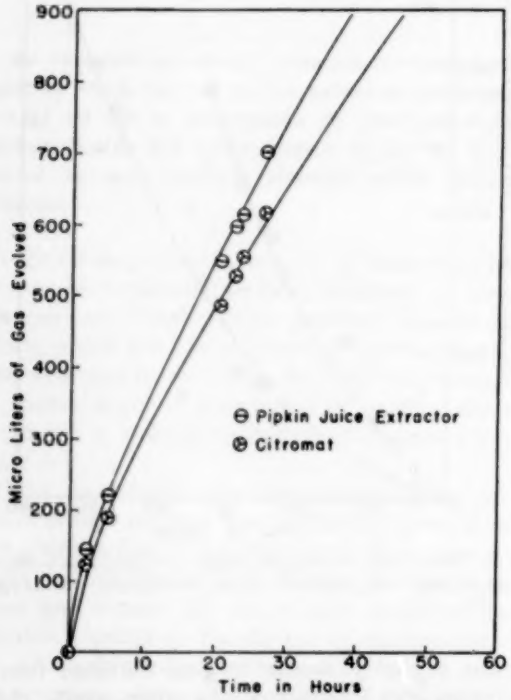


FIG. 4. Microliters of gas evolved from California coldpressed Valencia orange oil exposed to an atmosphere of nitrogen at 40° C. (104° F.).

accelerated oxidation tests under controlled conditions requiring the absorption of approximately 6,000 to 8,000 cu. mm. of oxygen per gram of oil." The experiments reported here do not verify their statement. The authors have found that an uptake of 1200 microliters of oxygen per gram of oil is sufficient to cause terpeney aromas in all cases. This difference of several thousand microliters may possibly be due to two factors: 1. The presence in Proctor and Kenyon's oil samples of a material more easily oxidized than the oil itself, which would result in higher oxygen uptake values, or 2, that the odor panel the authors used had a greater sensitivity for detecting the terpeney aroma

In the course of this investigation Florida oils were also placed under an atmosphere of hydrogen and it was observed that gas was evolved. These oils apparently underwent a chemical change but no apparent differences developed in the color or aroma of the oils. Although no explanation is offered at this time for the strange behavior of these oils when heated in an atmosphere of hydrogen, the data on gas evolution obtained is presented in Figure 5 as a matter of record.

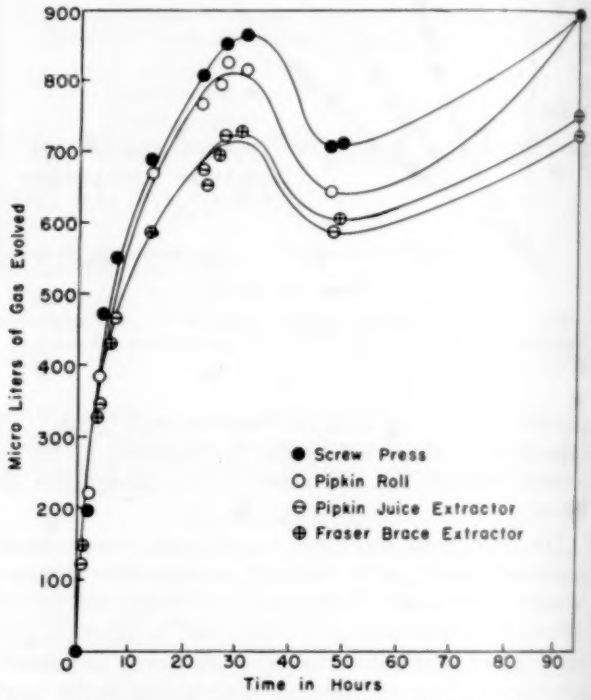


FIG. 5. Microliters of gas evolved from Florida coldpressed Valencia orange oil exposed to an atmosphere of hydrogen at 40° C. (104° F.).

SUMMARY

Further investigations on the oxidation of orange oil have indicated that previous techniques to evaluate the stability of the oil by measurement of oxygen absorption have not taken into consideration the evolution of gas from the oil. An improved manometric technique has been developed by which true oxygen uptake by coldpressed orange oil may be determined. This technique may be expected to give more realistic stability values. Coldpressed orange oil subjected to atmospheres of either nitrogen or hydrogen at 40° C. (104° F.) undergo a chemical reaction evolving gas. This reaction is apparently not harmful to the aroma or color of the oil.

LITERATURE CITED

1. KESTERSON, J. W., AND MCDUFF, O. R. Anti-oxidant studies. *Am. Perfumer Essent. Oil Rev.*, **54**, 285 (1949).
2. PROCTOR, B. E., AND KENYON, L. M. Objective evaluation of odor deterioration in orange oil. *Food Technol.*, **3**, 387 (1949).

Effect of Methods of Protection on Palatability of Freezer-Stored Meat[a]

R. L. HINER, A. M. GADDIS, AND O. G. HANKINS

Bureau of Animal Industry, Agricultural Research Administration, United States Department of Agriculture, Beltsville, Md.[b]

(Manuscript received August 28, 1950)

Deterioration in palatability of beef, pork, and lamb at freezer storage temperatures between —7.78° C. (18° F.) and —17.8° C. (0° F.) was due principally to oxidation of the fat. Except for desiccation, other changes noted in the fat and lean were not influenced by method of protection.

Meat preserved by freezing remains safe for consumption for many months. However, it gradually loses its quality, the rate depending, among other factors, on storage conditions.

The ideal goal in the preservation of meat by freezing is the development of methods of protection which will insure a product, at the end of a considerable period of time, which has undergone little or no deterioration of its original quality. Therefore it is important when comparing the results of different methods of protection to consider not only the length of time the meat may be kept in freezer storage before the onset of undesirability, but also the period of time a reasonable maintenance of the original quality is held. It is probably due to this "double standard" as well as to some differences in methods of assessing quality, that recommendations of investigators, as to the length of time meat may be stored in a frozen condition, have varied.

Dubois, Tressler, and Fenton *(3)* reported that pork became rancid in 2 months at —9.44° C. (15° F.), in about 4 months at —12.2° C. (10° F.), and showed signs of rancidity in 12 months at —17.8° C. (0° F.). Wellington, Mackintosh, and Vail *(13)* agreed that pork roasts stored at —13.9° to —7.78° C. (7° to 18° F.) should not have been held longer than 5 months. Hiner and Kauffman *(5)* found that exposed pork was unpalatable after 12 weeks at —7.78° C. (18° F.) and after 36 weeks at —17.8° C. (0° F.). Lard dipped pork was undesirable in 24 weeks at —7.78° C. (18° F.) and in 36 weeks at —17.8° C. (0° F.). Noble and Hardy *(7)* found that —9.44° C. (15° F.), —12.2° C. (10° F.), and —17.8° C. (0° F.) showed no difference in effectiveness in preserving the palatability of 24-hour ripened pork that was protected in moisture-vapor-proof wrapping. They postulate that pork cannot be stored at —17.8° C. (0° F.) to —9.44° C. (15° F.) for longer than 16 weeks to 22 weeks without having the flavor of fat and aroma decreased beyond the point of slight desirability. Pearce *(8)* concludes that for the best quality product, pork, presumably protected by moisture-vapor-proof wrapping, should not be stored longer than 3 weeks at —6.67° C. (20° F.), 8 weeks at —12.2° C. (10° F.), 26 weeks at —17.8° C. (0° F.), or 50 weeks at —23.3° C. (—10° F.).

Investigations by the U. S. Department of Agriculture *(12)*, Cook and White *(2)*, and Shrewsbury, Horne, Brown, Jordan, Milligan, Vestal, and Weitkamp *(11)*, indicate the desirability of storage at —17.8° C. (0° F.) or lower. Ramsbottom's *(9)* observations on meat stored for many years show that the primary changes at temperatures below —6.67° C. (20° F.) are due to oxidation of the fat. He concludes that the limiting factor is the cost of additional refrigeration necessary to maintain lower storage temperatures. However, if oxidation of the fat is truly the cause of loss in quality of meat, protection from the air should produce the desired results without resorting to lower temperatures. The purpose of the research reported here was to study the effect of exposure to and protection from air on meats when stored at low temperatures.

EXPERIMENTAL PROCEDURE

Choice, Good, and Commercial beef of dual-purpose Shorthorn steers fed a well-balanced ration were slaughtered at weights of approximately 900 pounds. Choice hogs fed a well-balanced fattening ration were slaughtered at about 225 pounds. Choice and Good spring lambs, creep fed on pasture, were slaughtered at weights of 80 to 100 pounds.

Beef loins and ribs were held in the cooler at 1° C. (34° F.) for 7 days and 20 days, pork loins for 5, 7, and 8 days, and lamb loins for 8 and 13 days. Storage samples were protected by wrapping in MSAT 300 cellophane, dipping in lard containing 0.1% of gum guaiac, and vacuum packing at a pressure of 28 inches of mercury in tin plate cans. Some samples were frozen and stored unprotected. Cellophane wrapped and vacuum packed samples were frozen after sealing while those protected with a coating of lard were frozen before the application of the dip coating. Storage temperatures for beef were —17.8° C. (0° F.); for pork —17.8° C. (0° F.) and —9.44° C. (15° F.); and for lamb, —17.8° C. (0° F.), —7.78° C. (18° F.) and —81.1° C. (—114° F.). Three or more samples from as many different animals were used for the controls, and for each storage condition at each storage period according to a statistical plan designed to eliminate error due to variation in the animals. Tables 1, 2, and 3 show the details of the various experiments on beef, pork, and lamb.

Control samples were tested at the time the meat was placed in storage. Cuts removed from storage were thawed at 7.22° C. (45° F.) for 24 hours. A sample of lean and a sample of separable fat were taken from each cut, combined with those of other cuts from the same storage conditions, ground, and stored in sealed mason jars in dry ice until chemical studies were made. Two lean samples were taken from the exposed cuts, that is, from the desiccated outside and from the inside. After chemical samples were taken, the cuts were roasted in a ventilated electric oven at 151.1° C. (302° F.) until an internal temperature of 60° C. (140° F.) for beef and 69.3° C. (156° F.) for pork and lamb was reached. The cooked meat was judged

[a] This paper was presented in part on November 27, 1948, at the annual meeting of the American Society of Animal Production held at Chicago, Illinois.

[b] H. Slofsky made the statistical analysis of the data; W. Kauffman determined the proximate composition of the meat; R. Berg, H. Tucker and R. Bechtold assisted in certain phases of the chemical work.

TABLE 1

Average Weight Loss of Beef Samples During Freezing, Storage, and Thawing as Affected by Methods of Protection.

Storage Conditions	Number of Samples	Days Aged	Weight loss after				
			12 weeks	24 weeks	36 weeks	48 weeks	82 weeks
First test —17.8° (0° F.)			%	%	%	%	%
1. Exposed	18	7	7.89	13.03	18.67	16.90 [e]	27.45
2. Vacuum packed	18	7	0.00	0.00	0.00	0.00	0.00
Second test —17.8° C. (0° F.)							
1. Exposed	9	20	5.86 [c]	6.20 [d]	.....	13.27	.....
2. Vacuum packed	9	20	0.00	0.00	.....	0.00	.....
3. Cellophane wrapped	9	20	1.49	1.85	.....	1.73	.....
4. Lard dipped	9	20	1.71	1.37	.....	1.76	.....

[c] 15 weeks of storage. [d] 31 weeks of storage. [e] 54 weeks of storage.

TABLE 2

Average Weight Loss of Pork Samples During Freezing, Storage, and Thawing as Affected by Methods of Protection.

Storage Conditions	Number of Samples	Days Aged	Weight loss after				
			12 weeks	24 weeks	36 weeks	48 weeks	82 weeks
First test —17.8° (0° F.)			%	%	%	%	%
1. Exposed	15	5	8.01	10.96	15.76	15.15 [h]	19.17
2. Vacuum packed	15	5	0.00	0.00	0.00	0.00	0.00
Second test —17.8° C. (0° F.)							
1. Exposed	16	7	5.61	10.32 [f]	11.51 [g]	13.92 [i]	.....
2. Vacuum packed	16	7	0.00	0.00	0.00	0.00	.....
3. Cellophane wrapped	16	7	2.02	2.13	1.72	2.09	.....
4. Lard dipped	16	7	0.53	0.90	0.56	1.08	.....
Third test —17.8° C. (0° F.)							
1. Exposed	12	8	4.66	4.10	7.98	14.67	.....
2. Vacuum packed	12	8	0.00	0.00	0.00	0.00	.....
3. Cellophane wrapped	12	8	1.59	1.12	0.72	3.58	.....
4. Lard dipped	12	8	1.18	0.68	2.12	2.27	.....
Third test —9.44° C. (15° F.)							
1. Exposed	12	8	7.90	14.66	17.40	22.28	.....
2. Vacuum packed	12	8	0.00	0.00	0.00	0.00	.....
3. Cellophane wrapped	12	8	2.50	3.03	2.76	5.40	.....

[f] 31 weeks of storage. [g] 39 weeks of storage. [h] 54 weeks of storage. [i] 51 weeks of storage.

by a panel of three experienced judges according to a modified six point scale (see Table 4) similar to that developed by the cooking committee of the Cooperative Meat Investigations Project *(1)*. Desirability of flavor of fat and lean, intensity of flavor of fat and lean, quality and quantity of juice, and tenderness were determined.

Various combinations of the following chemical analyses were made on raw lean and fat tissues. Moisture, protein, ether extract, and ash were determined on the lean by A.O.A.C. methods. Titratable acidity, pH, ammonia nitrogen, soluble nitrogen, Sorensen amino acid nitrogen, and non-protein nitrogen (tungstic acid) were determined on 5% sodium chloride extracts of the lean (250 ml. of 5% sodium chloride blended with 12.5 g. meat). The nitrogen results were calculated as percentage of total nitrogen. The percentage of free fatty acids as oleic and peroxides as milliequivalents per 1000 g. was determined by the methods of Jamieson *(6)* and Rockwood, Ramsbottom, and Mehlenbacker *(10)*, respectively. Measurements of fluorescence of lean tissue extracts were made with a 365 mμ filter-equipped Coleman photo-fluorometer on 10% sodium chloride (250 ml.) extracts of the lean (20.00 g.) against a quinine sulphate standard containing 0.3 mg. per liter of 0.1*N* H_2SO_4. Fluorescence values of lean tissue extracts were divided by the total nitrogen content to correct for variations in nitrogen content.

DEGREE OF DESICCATION

Tables 1, 2, and 3 show the average weight losses of beef, pork, and lamb samples during freezing, storing, and thawing. Exposed and cellophane protected samples stored at —9.44° C. (15° F.) or —7.78° C. (18° F.) had a much greater loss of moisture than those at —17.8° C. (0° F.). Vacuum-packed samples had no moisture loss. Generally, at all temperatures examined, the rate of desiccation was most rapid during the first 24 weeks of storage. Exposed pork was more resistant to moisture loss than exposed beef and lamb. However, when meat samples were protected by cellophane or lard dipping there was no significant difference in moisture loss between the different kinds of meat at a

TABLE 3

Average Weight Loss of Lamb Samples During Freezing, Storage, and Thawing as Affected by Methods of Protection.

Storage Conditions	Number of Samples	Days Aged	Weight loss after			
			12 weeks	24 weeks	36 weeks	48 weeks
First test —17.8° (0° F.)			%	%	%	%
1. Exposed	16	13	12.03	15.28	16.10	17.38
2. Vacuum packed	16	13	0.00	0.00	0.00	0.00
3. Cellophane wrapped	16	13	0.00	1.11	0.05	0.53
Second test —17.8° C. (0° F.)						
1. Exposed	16	8	12.08	20.03	19.46	23.10
2. Vacuum packed	16	8	0.00	0.00	0.00	0.00
3. Cellophane wrapped	16	8	0.81	1.68	0.89	1.67
Second test —7.78° C. (18° F.)						
1. Exposed	8	8	24.48	39.07	41.29	40.32
2. Vacuum packed	8	8	0.00	0.00	0.00	0.00
Second test—81.1° C. (—114° F.)						
1. Exposed	4	8	1.17	3.96	.....	.....
2. Vacuum packed	4	8	0.00	0.00	.....	.....

TABLE 4

Chart for Grading Meat for Palatability

Factor	Phase	Rating					
		6	5	4	3	2	1
Flavor of fat	Intensity	Very pronounced	Pronounced	Moderately pronounced	Slightly pronounced	Perceptible	Imperceptible
	Desirability	Very desirable	Desirable	Moderately desirable	Slightly desirable	Slightly undesirable	Undesirable
Flavor of lean	Intensity	Very pronounced	Pronounced	Moderately pronounced	Slightly pronounced	Perceptible	Imperceptible
	Desirability	Very desirable	Desirable	Moderately desirable	Slightly desirable	Slightly undesirable	Undesirable
Quality of juice	Intensity	Very rich	Rich	Moderately rich	Slightly rich	Perceptible	Imperceptible
Quality of juice	Intensity	Very juicy	Juicy	Moderately juicy	Slightly dry	Dry	Very dry
Tenderness	Intensity	Very tender	Tender	Moderately tender	Slightly tough	Tough	Very tough

given temperature. Cellophane and gum guaiac-treated lard were both satisfactory in protecting against desiccation. Small differences observed between the two kinds of protection are not consistent and probably are not significant.

ORGANOLEPTIC DATA

Organoleptic data were from 7 experiments which could not be suitably combined for inspection and statistical treatment because of the variable ripening periods. The amount of tabular material involved were therefore excessive. Since in all the experiments the greatest change was in the desirability of flavor of fat (apparently this factor was the chief cause of changes in desirability of flavor of lean, intensity factors, and quality of juice) it appeared that the changes and relationships of the palatability factors as affected by temperature and type of protection could be amply illustrated by the data from a single complete experiment for each kind of meat. Consequently, in Tables 5, 6, and 7, such data for beef, pork, and lamb, respectively, are given. The data were obtained by the algebraic subtraction of the average storage scores from the average control scores. Thus figures with a minus sign indicate a decrease, and those with a plus sign, an increase. The statistical analysis was made by the application of Fisher and Yates' *(9)* *t*-test of significance to the judges' scores. In order to illustrate the rate of decrease in quality as affected by ripening period, temperature of storage, and protection from air, the average scores for desirability of flavor of fat were plotted against time in storage (Figures 1, 2, 3, and 4).

The many factors involved which can cause variation make organoleptic data difficult to evaluate. Among sources of variation are differences in meat cuts, and unavoidable differences in the degree of doneness and sampling. It is generally recognized that the subjective method of determining palatability has serious drawbacks. Judges show different preferences, and these preferences vary from time to time. Moreover, few judges can discriminate well within narrow limits. Therefore scores can not be treated as true numbers. It was not possible to provide a fresh reference standard for each storage period. Consequently much de-

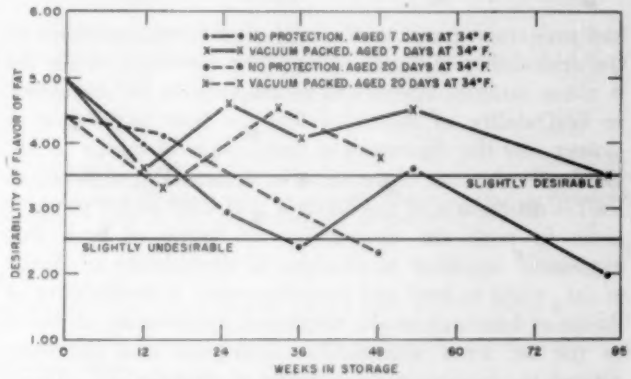


FIG. 1. Effect of protection from air and length of ripening and storage periods on desirability of flavor of fat of beef samples at a storage temperature of —17.8° C. (0° F.).

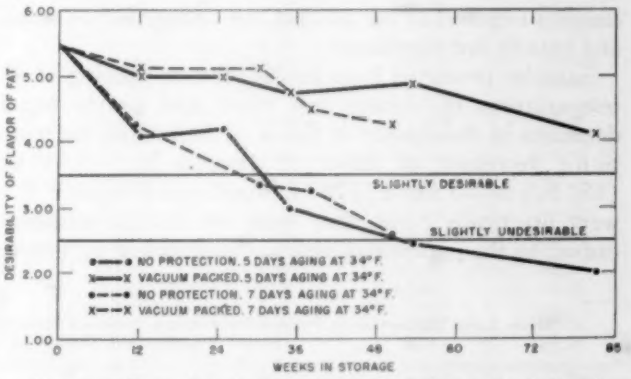


FIG. 2. Effect of protection from air and length of ripening and storage periods on desirability of flavor of fat of pork samples at a storage temperature of —17.8° C. (0° F.).

pended on the memory of the judge. This no doubt accounts for much of the anomolous results obtained in the trends of scores of the palatability factors. Hence it is very likely that the rate and degree of change in palatability factors indicated for a given type of protection are approximates. However, the comparisons obtained between the different types of protection in a period of storage are believed to be more nearly accurate.

Tables 5, 6, and 7 indicate that the major change was in the flavor of fat. Samples unprotected from the air

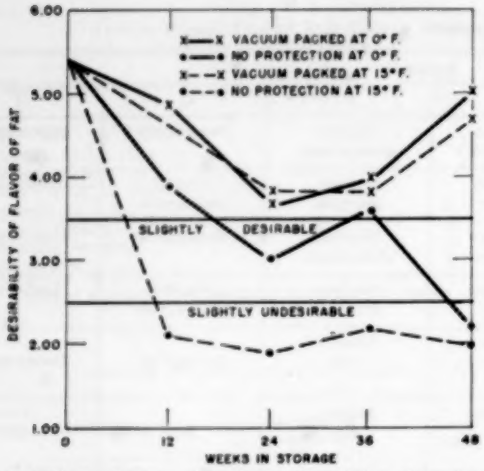


FIG. 3. Effect of protection from air and length and temperature of storage periods on desirability of flavor of fat of pork samples aged 8 days at 1° C. (34° F.).

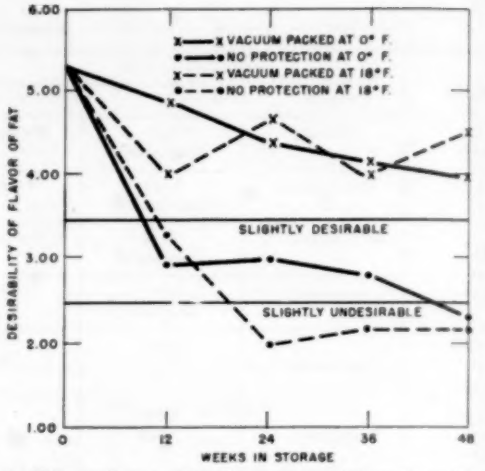


FIG. 4. Effect of protection from air and length and temperature of storage periods on desirability of flavor of fat of lamb samples aged 8 days at 1° C. (34° F.).

had progressive and statistically significant decreases in the desirability of flavor of fat. The condition of the fat in these samples appears to be responsible for decreases in desirability of flavor of lean as they parallel at a slower rate the decreases in desirability of flavor of fat. Evidently the rate of decrease in desirability of flavor of lean is a function of the amount and kind of fat present, since in pork the desirability of flavor of lean was extremely sensitive to changes in desirability of flavor of fat, while in beef and lamb decrease in desirability of flavor of lean was small. Increases in intensity of flavor of the fat were statistically significant and inversely related to changes in desirability of flavor of fat. There was a trend toward small increases in intensity of flavor of lean but these were not statistically significant. Quality of juice showed some tendency to decrease in samples exposed to the air, but the changes were small and usually not significant.

Samples protected from air by vacuum packing at all temperatures of storage had small and nearly equal decreases in desirability of flavor of the fat and the lean. Since decreases of flavor of samples at —9.44° C. (15° F.) or —7.78° C. (18° F.) and —17.8° C. (0° F.) were practically equal, they were not due to oxidation caused by the presence of residual amounts of oxygen in the container. Therefore, the apparent decreases in flavor may be due to some type of flavor reversion or to error in judging because of the absence of a fresh reference standard.

Moisture-vapor-proof coverings such as cellophane and lard dip gave nearly as good protection as vacuum packing for all factors except intensity and desirability of flavor. They apparently gave some slight protection from air. However, since the amount of air needed to product oxidation of the fat is relatively small, the effectiveness of moisture-vapor protection is probably not due to protection from the air. Evidently the drying process facilitates or speeds up fat oxidation in some way, possibly by enabling deeper penetration by the air.

Exposure resulting in a large amount of desiccation appeared to cause some decrease in desirability of flavor of the lean not attributable to fat oxidation, and decrease in tenderness and quantity of juice. However, on the whole changes in quantity of juice and tenderness were small.

Statistical analysis by the t-test of differences between exposed and vacuum-packed samples of lamb stored at —17.8° C. (0° F.) showed them to be highly significant in desirability of flavor of fat, intensity of flavor of fat, and quantity of juice.

TABLE 5

Mean Score Differences in Palatability Between Unstored Roasted Beef Samples[1] and Stored Samples Aged for 20 Days at 1° C. (34° F.) Before Freezing and Storage and the Significance of These Differences[2, 3]

Storage Conditions —17.8° C. (0° F.)	Desirability of Flavor		Intensity of Flavor		Juice		Tenderness
	Fat	Lean	Fat	Lean	Quality	Quantity	
15 weeks of storage							
Exposed	−0.31	+0.09	−0.61	−0.03	+0.44	+0.44	+0.42
Cellophane	−1.42*c*	−0.25	+0.04	−0.14	+0.22	0.00	−0.15
Lard dip	−0.86	−0.47	−0.50	−0.14	+0.44	+0.11	+0.19
Vacuum	−0.64	−0.47	+0.05	−0.03	+0.44*b*	+0.44	+0.08
32 weeks of storage							
Exposed	−1.31*b*	−0.80*b*	−0.17	−0.36	+0.11	−0.22	+0.31
Cellophane	−2.31*d*	−0.69*b*	+0.16	−0.14	+0.11	−0.67	−0.36
Lard dip	−1.31*b*	−0.58*b*	−0.06	−0.25	−0.22	−0.33	−0.25
Vacuum	+0.14	−0.14	−0.17	+0.19	+0.89*c*	−0.33	+0.75*d*
48 weeks of storage							
Exposed	−2.09*d*	−0.75*a*	0.00	−0.92	0.00	−1.33*c*	−0.25
Cellophane	−2.31*d*	−0.36	+0.15	−0.03	+0.22	−0.89	−0.14
Lard dip	−1.42*a*	−0.58*a*	−0.06	−0.03	+0.22	−0.22	−0.36
Vacuum	−0.64	−0.91*d*	+0.05	−0.03	−0.22	−1.22*c*	−0.36

[1] Mean control scores for desirability of flavor of fat 4.42 and of lean 5.58; for intensity of flavor of fat 5.17 and of lean 5.25; for quality of juice is 4.00 and of quantity 5.00; and for tenderness 5.25. [2] Small letter opposite mean score difference indicates probability value: *a*, less than 0.05; *b*, less than 0.02; *c*, less than 0.01; *d*, less than 0.001. [3] All conditions had 19 degrees except exposed at 48 weeks which had 16 degrees of freedom.

TABLE 6

Mean Score Differences in Palatability Between Unstored Roasted Pork Samples [m] and Stored Samples Aged 8 Days at 1° C. (34° F.) Before Freezing and Storage at —9.44° C. (15° F.) and at —17.8° C. (0° F.), and the Significance of these Differences.[n, o]

Storage Conditions	Desirability of Flavor		Intensity of Flavor		Juice		Tenderness
	Fat	Lean	Fat	Lean	Quality	Quantity	
12 weeks of storage							
Exposed, 15° F.	−3.28*d*	−0.98*c*	+0.69*b*	+0.19	−0.08	−0.29	−0.25
Cellophane, 15° F.	−2.17*d*	−1.09*c*	+0.03	−0.03	+0.14	+0.26	+0.09
Exposed, 0° F.	−1.52*d*	−0.53	+0.36*a*	+0.30	+0.14	−0.07	−0.02
Cellophane, 0° F.	−1.28*d*	−0.86*c*	+0.14	+0.08	−0.30	+0.04	+0.31
Lard dip, 0° F.	−1.17*d*	−0.53*a*	+0.69	−0.03	+0.03	+0.04	+0.20
Vacuum, 0° F.	+0.50	+0.25	+0.36	−0.14	+0.25	+0.37	+0.20
24 weeks of storage							
Exposed, 15° F.	−3.50*d*	−1.42*d*	+0.92*c*	+0.30	−0.30	+0.04	−0.69*a*
Cellophane, 15° F.	−3.39*d*	−1.20*d*	+0.69*b*	−0.25	+0.25	−0.74*c*	−1.02*d*
Vacuum, 15° F.	−1.56*d*	−0.59	+0.53	+0.25	+0.03	−0.46	−0.36
Exposed, 0° F.	−2.39*d*	−0.53	+0.47	+0.19	+0.14	+0.04	−0.36
Cellophane, 0° F.	−2.50*d*	−0.53*a*	+0.47	+0.08	+0.25	−0.07	−0.36
Lard dip, 0° F.	−2.61*d*	−0.64*b*	+0.69*b*	+0.08	+0.25	−0.63*a*	−0.25
Vacuum, 0° F.	−1.72*d*	−0.53	+0.25	+0.08	+0.03	−0.07	+0.09
36 weeks of storage							
Exposed, 15° F.	−3.22*d*	−2.42*d*	+0.36	+0.08	−0.41	−0.52	−0.91*c*
Cellophane, 15° F.	−3.28*d*	−1.98*d*	+0.69*b*	−0.25	−0.41	−0.52	−0.80*c*
Vacuum, 15° F.	−1.56*d*	−0.92*c*	+0.03	−0.25	−0.47	+0.04	−0.69*d*
Exposed, 0° F.	−1.83*d*	−0.98*c*	+0.36	−0.03	−0.41	+0.04	−0.13
Cellophane, 0° F.	−2.28*d*	−0.86*c*	+0.25	−0.03	−0.08	−0.07	−0.25
Lard dip, 0° F.	−2.50*d*	−2.03*d*	+0.03	−0.25	−0.30	−0.52	−0.91*c*
Vacuum, 0° F.	−1.50*d*	−0.86*c*	+0.03	−0.36	−0.64	−0.07	−0.69*a*
48 weeks of storage							
Exposed, 15° F.	−3.39*d*	−2.31*d*	+0.92*c*	+0.19	−1.08*b*	−1.29*d*	−1.47*d*
Cellophane, 15° F.	−3.50*d*	−1.64*d*	+1.03*d*	+0.19	−0.53	−0.74*b*	−1.25*d*
Vacuum, 15° F.	−0.72*b*	−0.25	+0.36	+0.08	−0.37	−0.63	1.02*d*
Exposed, 0° F.	−3.17*d*	−1.09*d*	+0.69*b*	+0.19	−0.41	−0.52	−0.69*b*
Cellophane, 0° F.	−2.72	−0.86*b*	+0.58*a*	+0.19	−0.41	−0.29	−0.80*c*
Lard dip, 0° F.	−2.72	−0.86*c*	+0.80*c*	+0.19	+0.03	+0.15	−0.47
Vacuum, 0° F.	−0.39	−0.09	+0.36	+0.08	−0.19	−0.18	−0.69*d*

[m] Mean control scores for desirability of flavor of fat is 5.39 and of lean, 5.42; for intensity of flavor of fat is 4.64 and of lean, 4.92; for quality of juice is 3.97 and of quantity, 3.96; and for tenderness, 5.69. [n] Small letter opposite mean score difference indicates probability value as given in footnote [k], Table 5. [o] All samples except —9.44° C. (15° F.) vacuum had 43 degrees of freedom. —9.44° C. (15° F.) vacuum had 40 degrees of freedom.

TABLE 7

Mean Score Differences in Palatability Between Unstored Roasted Lamb Samples [p] and Stored Samples Aged 8 Days at 1° C. (34° F.) Before Freezing and Storage at —7.78° C. (18° F.), —17.8° C. (0° F.), and —81.1° C. (—114° F.) and the Significance of these Differences.[q, r]

Storage Conditions	Desirability of Flavor		Intensity of Flavor		Juice		Tenderness
	Fat	Lean	Fat	Lean	Quality	Quantity	
12 weeks of storage							
Exposed, 18° F.	−2.00*d*	−0.50	+0.42	−0.08	0.00	−0.58	+0.50
Vacuum, 18° F.	−1.33*a*	+0.17	+0.58	+0.42	−0.16	−0.91*b*	+0.50
Exposed, 0° F.	−2.41*d*	−0.75	+0.50	+0.08	−0.16	−0.58*c*	+0.83*a*
Cellophane, 0° F.	−2.08*d*	−0.25	+0.67*c*	+0.50*b*	−0.08	−0.75	+0.33
Vacuum, 0° F.	−0.41	0.00	−0.08	+0.50*b*	−0.33	+0.25*c*	+0.25
Exposed, —114° F.	−2.33*d*	−0.33	+1.16	+0.25	−0.33	−0.75*c*	+0.50*b*
Vacuum, —114° F.	−1.33*a*	+0.17	+0.25	+0.25	−0.33	−0.25	+0.50
24 weeks of storage							
Exposed, 18° F.	−3.33*d*	−1.66*d*	+1.58	+0.58	−2.00*d*	−2.25*d*	−0.50
Vacuum, 18° F.	−0.67	−0.16	+0.08	+0.08	−0.16	−0.75	−0.33
Exposed, 0° F.	−2.33	−1.41*c*	+1.58	+0.50*b*	−1.16*c*	−1.16*d*	−0.25
Cellophane, 0° F.	−1.00*d*	−0.83	+0.33	+0.50*b*	0.00	−0.58	+0.17
Vacuum, 0° F.	−0.91	+0.17	+0.17	+0.08	−0.16	−0.08	+0.50*a*
Exposed, —114° F.	−1.00*a*	+0.34	−0.42	+0.42	+0.17	−0.41*c*	+0.50
Vacuum, —114° F.	−0.16	+0.17	+0.25	+0.25	+0.17	−1.08*d*	−0.17
36 weeks of storage							
Exposed, 18° F.	−3.16*d*	−1.50*c*	+1.25*c*	+0.08	−0.05	−1.08*c*	+0.33
Vacuum, 18° F.	−1.33*b*	−0.33	+0.42	+0.25	+0.67	+0.42	+0.55
Exposed, 0° F.	−2.50*d*	−1.00*c*	+0.67*b*	+0.25	−0.41	−0.66*b*	−0.33
Cellophane, 0° F.	−1.66*d*	−0.08	+0.58	+0.25	−0.08	−0.08	0.00
Vacuum, 0° F.	−1.16*c*	0.00	+0.25	+0.33	+0.17	0.00	+0.08
48 weeks of storage							
Exposed, 18° F.	−3.16*d*	−1.83*c*	+1.25*d*	+0.58	−1.33	−2.25*d*	−0.17
Vacuum, 18° F.	−0.83	+0.17	+0.08	+0.08	+0.34	+0.75*b*	+0.33
Exposed, 0° F.	−3.00*d*	−0.08	+1.25*d*	+0.25	−0.08	−1.08*c*	−0.58
Cellophane, 0° F.	−1.75*d*	+0.17	+0.08	+0.58*b*	+0.34	+0.25	−0.33
Vacuum, 0° F.	−1.33*c*	+0.09	+0.17	+0.17	+0.17	0.00	+0.17

[p] Mean control scores for desirability of flavor of fat is 5.33 and of lean 5.33; for intensity of flavor of fat is 4.75 and of lean, 4.75; for quality of juice is 4.33 and of quantity, 4.58; and for tenderness, 5.50. [q] Small letter opposite mean score difference indicates probability value as given in footnote [k], Table 5. [r] Samples at —7.78° C. (18° F.) and —81.1° C. (—114° F.) had 16 degrees of freedom. Samples at —17.8° C. (0° F.) had 22 degrees of freedom.

The above analysis indicates that of the seven palatability phases studied, the desirability of flavor of fat is the most sensitive and representative of the changes taking place in meat stored in the freezer between the temperatures of —7.78° C. (18° F.) and —17.8° C. (0° F.).

Palatability Life of Freezer-stored Meat. As indicated earlier, one of the standards for meat preservation that should be considered is the length of time that meat may be kept in a palatable condition. For any given method of protection, except possibly vacuum-packed, meats stored at —17.8° C. (0° F.) were generally

superior to those stored at —9.44° C. (15° F.) and —7.78° C. (18° F.). See Figures 3 and 4 and Tables 6 and 7. The period of ripening, especially in unprotected samples, proved to be an important factor influencing the length of time meat cuts remained palatable in freezer storage, determined, in the present study, by the time elapsing before the desirability of flavor of fat reaches a rating of 2.50 (slightly undesirable) in the scale of 6, 5, 4, 3, 2, and 1. At —17.8° C. (0° F.) exposed cuts of beef (Figure 1), pork (Figure 2), and lamb (Figure 4) which had been held 7, 5, and 8 days, in the cooler were slightly undesirable in flavor of fat after about 69, 53, and 44 weeks of storage, respectively. However, with 20, 8, and 13 day ripening periods (Figures 1 and 3 for beef and pork) slight undesirability in flavor of fat occurred at 44, 45, and 34 weeks, respectively. At —9.44° C. (15° F.) exposed pork previously ripened for 8 days was considered unpalatable at 10.5 weeks. When ripened for 8 days, exposed lamb was slightly undesirable in fat flavor after about 20 weeks at —7.78° C. (18° F.). Thus pork which remained palatable as long or longer than lamb at —17.8° C. (0° F.) became undesirable sooner at higher temperatures. This, no doubt, is due not only to a difference in the chemical composition of the fat but also to a more active lipoxidase present in pork tissue.

Protection with cellophane and gum guaiac-treated lard generally resulted in a somewhat longer palatability life. At —17.8° C. (0° F.) cellophane protected beef, pork, and lamb ripened respectively at 20, 8, and 13 days, were still desirable in flavor of fat at 48, 51, and 48 weeks. At the same temperature of storage cellophane protected lamb aged 13 days was slightly undesirable in flavor of fat at 19 weeks. There was little significant difference between cellophane and lard dip protection. At the end of storage all vacuum packed cuts were generally still moderately desirable or better in fat flavor.

Maintenance of Original Quality. The second standard for meat preservation to be taken into consideration is the length of time the meat maintains its original quality in storage. In this study the original quality was considered to be upheld as long as the desirability of flavor of fat remained above a rating of 3.50 (moderately desirable). It was found that there was a rapid decline in quality in exposed and cellophane-protected samples. See Tables 5, 6, and 7. The data do not show a clear cut difference in rate of decrease in desirability of flavor of fat between exposed samples and those protected only from loss of moisture. At —17.8° C. (0° F.) the rating generally went below 3.50 between the 12th and 30th week, while at —9.44° C. (15° F.) and —7.78° C. (18° F.) this standard was passed before the 12th week. On the other hand, vacuum-packed samples lost quality at a very slow, and possibly not significant, rate. Vacuum-packed pork and lamb at —9.44° C. (15° F.) and —7.78° C. (18° F.) were moderately desirable or better in flavor of fat throughout storage and were considered nearly as good as vacuum-packed samples stored at —17.8° C. (0° F.). Vacuum-packed pork at —17.8° C. (0° F.) was decidedly better at 54 weeks than the exposed pork at 12 weeks, and fully as good at 82 weeks as the exposed pork at 12 weeks. Vacuum-packed lamb stored at —17.8° C. (0° F.) for 48 weeks was as good as it was at 12 weeks. Vacuum-packed beef at —17.8° C. (0° F.) was rated nearly as good after 83 weeks as at 12 weeks.

Evidently deterioration of the flavor of fat may be effectively controlled by vacuum packing. The maintenance of desirability of flavor of fat above the rating of 3.50 indicates that deterioration in quality which takes place rather rapidly when exposed to the air at these temperatures is due mostly to oxidation of the fat. It appears that vacuum-packed meats may therefore be stored at temperatures as high as —7.8° C. (18° F.) for well over a year and remain very acceptable substitutes for fresh meats.

The data for pork cuts not protected from the air agree well with Pearce's *(12)* conclusions as to the length of time pork may be stored at —6.67° C. (20° F.), —12.2° C. (10° F.), and —17.8° C. (0° F.) for the best quality product.

CHEMICAL CHANGES IN THE LEAN

In addition to moisture, fat, and protein analyses, various combinations of the determinations given under the experimental procedure were made on the raw separable lean. These analyses give the composition and the degree of proteolysis and amount of soluble protein nitrogen denaturation which took place in the lean tissue. These data, together with the organoleptic material, make an amount of tabulation too great to include in this paper. These analyses showed insignificant changes and are not given here because of the conclusion from the organoleptic data that there is little change in flavor due to the protein part of the lean.

Chemical changes observed in the lean tissue, with the possible exception of those produced by desiccation, do not appear to be related to the type of protection used. Some slight changes are apparently due to differences in temperature of storage. At —9.44° C. (15° F.) and —7.78° C. (18° F.) a very small amount of proteolysis took place as shown by slight increases in the percentage of non-protein nitrogen and Sorensen amino acid nitrogen. Longer intervals of ripening in the cooler before freezing resulted in a higher initial percentage of soluble, non-protein and amino acid nitrogen. In general, little change took place in pH, percentage of ammonia nitrogen, and titratable acidity. The chief change in the lean tissue during storage was a progressive decrease in soluble protein nitrogen. This decrease is presumably due to denaturation and apparently was not influenced by the difference in temperatures of storage used nor by exposure to the air. The outside desiccated portion of exposed samples underwent a large and significant decrease in soluble protein nitrogen. It is regrettable that this portion was not tested for palatability. In general, although protein denaturation may be related to loss in quality of the lean, it evidently is an unimportant factor in comparison with the influence of the fat. Fluorescence of 10% sodium chloride extracts of the lean tissue of pork and lamb stored at —17.8° C. (0° F.), —9.44° C. (15° F.), and —7.88° C. (18° F.) tended to increase during storage. However, there were no significant differences between types of protection or temperatures.

CHEMICAL CHANGES IN THE FAT

The conclusion was reached from the palatability data that oxidation of the fat is chiefly responsible for decline in quality of freezer-stored meats. This is supported by the observation that the greatest change in the fat was an increase in peroxides. There was little change in the percentage of free fatty acids except for a small tendency to increase at temperatures of —9.44° C. (15° F.) and —7.78° C. (18° F.). However, the increase was not influenced by the kind of protection. Clearly, fat hydrolysis is not a factor at the temperatures studied. Moveover, it is evident that little breakdown of peroxides into acids occurred.

Peroxide values of vacuum-packed samples were generally lowest in their respective temperature groups (Table 8). In most cases, the —9.44° C. (15° F.) and

TABLE 8

Desirability of Flavor Scores, and Peroxide Values of Pork and Lamb Fat After 48 Weeks of Storage

Kind of Fat and Storage Conditions	Score for Desirability of Flavor*	Peroxide Value Milliequivalents per 1,000 g.
Pork		
Exposed at 15° F.	2.00	15.63
Cellophane wrapped at 15° F.	1.89	65.38
Vacuum packed at 15° F.	4.67	3.49
Exposed at 0° F.	2.22	17.37
Cellophane wrapped at 10° F.	2.67	11.06
Lard dipped at 0° F.	2.67	17.90
Vacuum packed at 0° F.	5.00	0.54
Lamb		
Exposed at 18° F.	2.17	1.45
Vacuum packed at 18° F.	4.50	1.02
Exposed at 0° F.	2.33	0.72
Cellophane wrapped at 0° F.	3.58	0.76
Vacuum packed at 0° F.	4.00	0.39

* See Table 4, "A Chart for Grading Meat for Palatability."

—7.78° C. (18° F.) samples as a group had higher values than those stored at —17.8° C. (0° F.), although the vacuum-packed samples were practically equal in desirability of flavor of fat. However, at one temperature of storage there is a fair qualitative agreement in most cases with desirability of flavor of fat scores. Undesirability of flavor of fat appeared in connection with low peroxide values in lamb and with relatively high values in pork fat.

The use of peroxide value is the best method known for determining the amount of oxidation which has taken place in a fat. However, peroxides are not directly responsible for undesirable flavors as they are practically tasteless when pure. The bad flavors are produced by decomposition products of the peroxides. Therefore a better objective index might result from the estimation of one or more of the peroxide breakdown compounds. Work is in progress in this laboratory on the development of such methods.

SUMMARY

Beef, pork, and lamb cuts, ripened various periods of time, were stored exposed, cellophane-wrapped, lard-dipped, and vacuum-packed at —7.78° C. (18° F.), —9.44° C. (15° F.), —17.8° C. (0° F.) and —81.1° C. (—114° F.). Samples were removed at intervals, cooked by standard methods, and rated organoleptically.

Desiccation of exposed frozen stored meat was retarded by a high fat content of muscle tissue and by a low storage temperature. Cellophane and lard coating were equally satisfactory practical protectants against desiccation. Vacuum packing resulted in no moisture loss. Deterioration in palatability at temperatures from —7.78° C. (18° F.) to —17.8° C. (0° F.) have been shown to be due primarily to oxidation of the fat resulting in a progressive decrease in the desirability of flavor of that component. This caused a decrease in the desirability of flavor of the lean, quality of juice, and a small increase in the intensity of flavor of the lean to an extent evidently dependent on the concentration of fat in the lean. Desiccation appeared to cause some decrease in lean flavor, desirability, and juiciness. Desirability of flavor of fat was the best subjective index of quality among the palatability factors studied. The length of time meat could be kept in freezer storage before it became unpalatable (desirability of flavor of fat, 2.50) was increased by shortening the ripening period, lowering the temperature of storage, or by protecting from the air. Cellophane wrapping and lard dipping gave a small amount of protection against oxidation. Original quality of the meat, as judged by the maintenance of a moderately desirable flavor of fat (rating of 3.50) or above, declined rapidly in all types of protection studied except vacuum packing. Vacuum-packed samples did not go below the standard of 3.50 in these experiments.

Chemical changes noted in the muscle tissue appeared to have little relation to palatability changes. Fat hydrolysis was negligible. Peroxide values gave fairly good correlation of a qualitative nature with desirability of flavor of fat, especially when one temperature of storage was considered.

LITERATURE CITED

1. Alexander, L. M., Clark, N. G., and Howe, P. E. Methods of cooking and testing meat for palatability. Supplement to national project of the Cooperative Meat Investigations. 1933, U. S. Dep. Agr. Bureaus of Home Economics and Animal Industry, Mimeographed, 15 pp.
2. Cook, W. H., and White, W. H. Effect of temperature and humidity on color of lean and development of rancidity in the fat of pork during freezer storage. *Can J. Research*, **19D**, 53 (1941).
3. DuBois, C. W., Tressler, D. K., and Fenton, F. Influence of rate of freezing and temperature of storage on quality of frozen meat. *Proc. Food Conf. Inst. Food Technol.*, **1**, 167 (1940).
4. Fisher, R. A., and Yates, F. *Statistical Tables for Biological, Agricultural and Medical Research*. 1938, Oliver and Boyd, London.
5. Hiner, R. L., and Kauffman, W. R. Coating of fat protects meat against freezer burn. *Food Inds.*, **16**, 275 (1944).
6. Jamieson, G. S. *Vegetable Oils and Fats*. 1932, The Chemical Catalogue Co., Inc., New York, N. Y., 324 pp.
7. Noble, I., and Hardy, F. Effect of storage temperature and time upon quality of pork preserved by freezing. *Food Research*, **10**, 165 (1945).
8. Pearce, J. A. Factors affecting quality of frozen pork. *Can. Food Inds.*, **19**, 18 (1948).
9. Ramsbottom, J. M. Freezer storage effect on fresh meat quality. *Refrig. Eng.*, **53**, 19 (1947).
10. Rockwood, B. N., Ramsbottom, J. M., and Mehlenbacker, V. C. Preparation of animal tissue fat for determination of peroxides and free fatty acids. *Ind. Eng. Chem., Anal. Ed.*, **19**, 853 (1947).
11. Shrewsbury, C. L., Horne, L. W., Brawn, W. Q., Jordan, R., Milligan, O., Vestal, C. L., and Weitkamp, N. E. Chemical, histological, and palatability changes in pork during freezing and storage in the frozen state. Purdue Univ. Agr. Exp. Sta. *Bull.*, 472 (1942).
12. U. S. Dep. Agr. Chief of Bureau of Animal Industry Reports (1938-48).
13. Wellington, G. H., Mackintosh, D. L., and Vail, G. E. Pork storage in freezer lockers. Trans. Kansas Acad. Sci., **43**, 313 (1940).

Frozen Cooked Rice

MILDRED M. BOGGS, CATHERINE E. SINNOTT, O. R. VASAK, AND E. B. KESTER
Western Regional Research Laboratory, Albany, California*

(Manuscript received January 4, 1951)

Frozen cooked rice was prepared by slowly boiling the rice in a small amount of water for 10 minutes and then steaming it for an additional 25 minutes, air cooling, packaging in cellophane, and freezing. It was stored for 1 week, 2 months, and 8 months at —23, —18.5 and —12° C. (—10, 0, and 10° F.). Following storage the rice was prepared for the table in 10 minutes. Polished Texas Patna and California Pearl rice were used in the study. Tasters found the frozen rice fully equal to freshly cooked rice in every respect, even after 8 months of storage at —12° C. (10° F.). Estimates of manufacturing costs indicate that a 12-oz. carton of frozen cooked rice could be sold on the retail market for about 13 to 15 cents.

The purpose of the work reported here was to develop frozen cooked polished rice, fully equal in eating quality to the freshly cooked product, that could be prepared for the table in ten minutes or less, and to investigate its behavior in freezing storage.

Frozen properly cooked rice, provided it maintains acceptable quality during storage, might become an attractive retail sales item. Many housewives have difficulty preparing rice to bring out its excellent qualities, and may not have sufficient experience to understand and compensate for the differences between long and short grain types; as a result, their culinary efforts often yield dishes less palatable than they might be. Frozen rice would also have an appeal from the standpoint of convenience and saving of time.

Studies of the type reported here carry the inference that only one ideal cooked product is known. This, of course, is not true. Preferences among a group of individuals for different flavors and textures in the same food are well known. A number of persons from outside the Laboratory personnel indicated that they liked "sticky" rice. Some Orientals, according to Vinacke, Hartzler, and Tanada *(1)* object to processed or parboiled rice because they can not manipulate it with chop sticks or make it into balls. In general, however, rice with well-separated grains seems to be preferred.

Standards of excellence for cooked rice in the present study were established by a group of Laboratory staff members including several Orientals, others who had lived in the Orient, and still others who had had no Oriental influence.

Preparation of the frozen cooked rice included the following steps: (1) Cooking the rice to a slightly underdone stage, (2) partially cooling in air, (3) packaging in cellophane and heat sealing, (4) freezing at —23° C. (—10° F.), and (5) reheating for 10 minutes just prior to serving. Effect of storage of 1 week, 2 and 8 months each at —23, —18.5, and —12° C. (—10, 0, and 10° F.) were investigated. A long grain rice (Texas Patna) and a short grain rice (California Pearl) were used. Following each storage period the frozen cooked samples were compared by tasters with two freshly cooked long grain and short grain samples prepared from dry rice stored at room temperature and at —34.5° C. (—30° F.).

EXPERIMENTAL

Scoring. Fifteen persons selected from the Laboratory staff served on the taste panel but usually only ten of them were present on a given day. Six were Orientals and two others had lived in the Orient for long periods. The remaining seven had no special experience but they were able to qualify for the panel.

The factors scored were color, separation of grains, flavor, and texture. Score 7 indicated very white rice, well separated grains, typical rice flavor and no off-flavor, and very desirable texture in the mouth. Score 1 indicated discolored rice, very poor separation of grains, much off-flavor and very undesirable texture. Intermediate quality ratings were expressed by units in the 1-7 scale. Because texture includes many qualities, tasters were asked to check terms that denoted undesirable characteristics: too dry, too firm, too moist, too sticky, too soft, and slimy. Tasters could use other descriptive terms, but seldom did so.

Each test set was scored five times at each storage period. All long-grain samples including the freshly cooked controls were scored together. The same was true for the short-grain samples but the panel was not served both long- and short-grain rices on the same day. Daily average scores of all tasters were analyzed by the variance and least-difference procedures.

Preparation of the Rice. To evaluate the principal factors determining eating quality of rice, attention was given to the effect of washing the rice prior to cooking, amounts of water used during cooking, and the method and time of cooking.

Thorough washing of the rice prior to cooking slightly decreased its stickiness. There was little difference in quality, whether the rice was cooked full time over direct heat with a small amount of water or part time in a steamer. The latter, however, was more convenient. The full-time direct-heat method always produced a scorched layer in the bottom of the pan when the rice was cooked to a sufficiently dry stage. This effect is typical of the so-called Chinese method but was too difficult to control for use in the present study. In the final procedure, the rice was slowly boiled until barely dry, then placed in a home-type steamer and cooked for the additional time required as noted below. Variations in cooking time of about 10 minutes had little influence on quality, but the amount of water for a given cooking time had a great influence on texture and grain separation.

The detailed cooking procedure used in this study follows: Three-fourths cup (148 g.) of rice was quickly washed four times. The bulk rice used was slightly dirty, and some washing was needed. In view of vitamin and mineral losses during washing reported by Vinacke et al. *(1)*, a single washing would have been preferable. The drained rice and optimum amount of cold water were brought to the boiling point, stirred once, and then slowly boiled in a tightly covered pan for 10 minutes without further stirring. Two-thirds cup (148 ml.) of water was used

* Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Report of a study made under the Research and Marketing Act of 1946.

with short-grain rice to be frozen, but three-fourths cup (185 ml.) for long-grain rice to be frozen and for both samples to be served immediately. Following boiling, the partially cooked rice was placed in the food compartment of a preheated gallon steamer, with space around the edges for entry of the steam. Rice to be frozen was steamed for 25 minutes and that to be served immediately (control sample), 35 minutes. The rice was not stirred, and vigorous boiling of water was maintained during steaming. The formula yielded about 360 g. (0.8 lb.) of cooked rice, giving a 2.4-fold increase in weight during cooking.

The rice to be frozen was cooled on trays in air, packaged in cellophane bags and heat sealed, then frozen in rapidly circulating air at —23° C. (—10° F.), and stored at —23, —18.5, and —12° C. (—10, 0, and 10° F.). Just prior to tasting, the solidly frozen rice was placed in the preheated steamer, thawed, and reheated over rapidly boiling water. The time required was 10 minutes.

The cooked samples were held for a maximum of 30 minutes between cooking and scoring. To minimize changes in the rice during this period, low heat was used, two layers of muslin were inserted between the water and food compartments of the steamer to exclude steam, and the cover was removed from the upper vessel.

RESULTS

The average scores for all samples are reported in Table 1. The differences between scores of any line in the table are too small to be considered of practical importance. In many instances, however, the differences were statistically significant and they almost invariably favored frozen rice. It may be concluded therefore that from a palatability standpoint frozen cooked rice after 8 months of storage at —12° C. (10° F.) is at least as good as, and perhaps slightly better than, freshly cooked rice.

TABLE 1

Scores for Stored Rice

Rice	Storage period	Average Scores [b]					Least significant difference at 1% level
		Dry rice stored at		Frozen cooked rice stored at			
		room temp.	—30° F.	—10° F.	0° F.	10° F.	
Color							
Patna	1 wk.	6.3	6.4	6.7	6.6	6.7	0.2 [c]
Patna	2 mo.	5.7	5.9	6.6	6.5	6.7	0.3
Patna	8 mo.	6.2	6.7	7.0	7.0	7.0	0.2
Pearl	1 wk.	6.2	6.2	6.4	6.5	6.4	0.3
Pearl	2 mo.	5.9	6.1	6.2	6.2	6.2	0.3
Pearl	8 mo.	6.5	6.6	6.7	6.7	6.7	0.2
Grain Separation							
Patna	1 wk.	6.1	5.8	6.4	6.6	6.4	0.3
Patna	2 mo.	6.0	5.8	6.0	6.2	6.1	....
Patna	8 mo.	6.2	5.9	6.2	6.2	6.2	....
Pearl	1 wk.	5.2	5.2	5.4	5.5	5.2	....
Pearl	2 mo.	4.8	4.8	5.5	5.3	5.5	0.3
Pearl	8 mo.	5.2	5.1	5.6	5.4	5.2	0.4
Flavor							
Patna	1 wk.	6.7	6.7	6.7	6.7	6.7	....
Patna	2 mo.	6.6	6.6	6.6	6.7	6.5	....
Patna	8 mo.	6.4	6.6	6.5	6.5	6.3	....
Pearl	1 wk.	6.6	6.6	6.5	6.7	6.6	0.2
Pearl	2 mo.	6.4	6.3	6.5	6.4	6.5	....
Pearl	8 mo.	6.6	6.7	6.7	6.7	6.5	....
Texture							
Patna	1 wk.	5.7	5.7	6.3	6.3	6.2	0.4
Patna	2 mo.	5.6	5.8	6.4	6.4	6.4	0.4
Patna	8 mo.	5.8	6.0	6.2	6.4	6.3	0.5
Pearl	1 wk.	5.0	5.1	5.5	5.6	5.3	0.6
Pearl	2 mo.	5.3	5.3	5.8	5.7	5.6	0.3
Pearl	8 mo.	5.5	5.4	5.8	5.9	5.5	0.4

[b] Highest scores indicate best quality, with 7 as maximum.

[c] This least significant difference value of 0.2 means that a difference of 0.2 between two scores in this row is probably real and not due to chance.

The slightly whiter color of the frozen cooked rice may be due to a surface effect. It seems unlikely that there would be a change in pigment during freezing or freezing storage. The texture difference is not surprising when one considers the variation in the treatment received by the frozen rice: freezing, thawing, and reheating. Freezing alone changes the texture of many foods. Such changes, however, are usually undesirable instead of favorable.

The samples stored at —23, —18.5 and —12° C. (—10, 0, and 10° F.) did not differ significantly from each other in quality. Apparently cooked polished rice can tolerate higher storage temperatures than most foods. It was also observed that the dry rice stored at room temperature showed no organoleptic differences from the sample stored at —34.5° C. (—30° F.) after cooking.

In a few instances the scores for a given sample stored for different periods seem inconsistent. For example, color scores for Patna rice stored at room temperature for 1 week, 2, and 8 months were 6.3, 5.7, and 6.2, respectively. It is unlikely that color first darkened and then became light again with increasing storage time. Such small differences scored months apart between storage periods are never considered reliable in this Laboratory because tasters cannot duplicate quality scores after long lapses of time. Usually we consider it satisfactory to determine which procedure is best when products must be stored for a given period. If a direct comparison of storage periods is desired, we use a different experimental plan.

The descriptive terms checked by tasters are summarized in Table 2. Since the 3 storage periods for any one sample gave essentially the same results, they are combined in the table. Any term that was checked less than 10% of the time for any sample was omitted.

TABLE 2

Percent of Judges Who Checked the Various Terms Describing Texture of Stored Rice [d]

Storage Conditions	Percent of Judges Who Checked [e]				
	Too dry	Too firm	Too moist	Too sticky	Soft
Patna Rice					
Dry rice stored at room temperature	27	49	0	2	2
Dry rice stored at —30° F.	19	37	4	4	5
Frozen cooked rice stored at —10° F.	8	6	8	0	18
Frozen cooked rice stored at 0° F.	6	6	6	1	9
Frozen cooked rice stored at 10° F.	8	8	5	2	11
Pearl Rice					
Dry rice stored at room temperature	13	18	10	44	7
Dry rice stored at —30° F.	11	16	9	46	8
Frozen cooked rice stored at —10° F.	9	6	7	39	4
Frozen cooked rice stored at 0° F.	8	9	8	30	2
Frozen cooked rice stored at 10° F.	8	14	11	39	4

[d] Results for all storage periods combined, since the periods were essentially alike.

[e] 169 total judgments for Patna and 158 for Pearl rice.

Although the method selected for freshly cooked Patna rice gave the highest scores and fewest check marks of any method tried, the freshly cooked sample was considered to be too dry and too firm when compared with the frozen rice (Table 2). Also a small number of tasters considered the frozen cooked rice too soft. Neither of these situations could be corrected without impairing some other quality factor.

Many of the tasters (although less than half) rated the Pearl rice too sticky. This seems to be characteristic of the variety. Hundreds of samples were cooked by different procedures in an effort to find a method that would overcome this defect, but no such method was found.

DISCUSSION

Frozen cooked rice, both Patna and Pearl, prepared by the procedures described herein, is considered a product of excellent quality. It hardly seems necessary to mention that good results cannot be expected if the rice is poorly cooked before it is frozen. Subjective appraisal of quality factors was sufficiently consistent throughout the study to indicate that taste-panel scoring is adequate for the determination of quality of cooked rice. No adverse problems were encountered that might detract from the practical importance of this work and its application to large-scale manufacture, with the possible exception of mechanical handling and packaging of cooked rice. However, such problems have been met and solved with similar products. An investigation similar to that reported herein, concerned with brown and parboiled rice, is in progress at this Laboratory.

Cost Studies. The probable costs of preparation of frozen cooked rice have been estimated to serve as a guide to the commercial feasibility of the product. The process used as a basis is the one described above for long-grain rice. Capital investment requirements for plants having capacities of 1500, 4500, and 9000 pounds of frozen product per hour were estimated to be $75,000, $150,000, and $260,000, respectively.

In this study it is assumed that rice cooking plants would be built adjacent to, and operated in conjunction with, other established food processing plants and that cooked packaged rice would be transported to a refrigerated warehouse for custom freezing and storage. The unit costs are based on an annual operation of 240 10-hour shifts.

In a commercial application of the laboratory procedure, rice probably would be removed from storage by bucket conveyor and washed in a rod-reel washer. Next, it would be conveyed by belt to hoppers and measured into stainless-steel jacketed kettles equipped with removable wire-lined baskets. Water would be added in the proportion of 1.28 pounds per pound of dry rice, and the mass boiled. Following complete absorption of water, the basket of partially cooked rice would be lifted out of the kettle by hoist and dumped into a hopper, which would feed the rice into a steamer for completion of cooking. The steamer would be one similar to a large blancher in general design, equipped with stainless-steel mesh belts.

Following cooking, the rice would be discharged on a stainless-steel mesh belt (to allow draining) conveyed through an air blast cooler and cooled to approximately room temperature, and then packaged in 12-oz. cardboard cartons. The latter would be transported to a refrigerated warehouse where they would be frozen and held in storage until marketed.

Facilities for one week's storage of dry rice are assumed to be adequate for the proposed operations. In the calculations, the bulk densities of raw and cooked rice are taken as 36 and 43 pounds per cubic foot, respectively. The cost of long-grain rice is assumed to be 11 cents per pound, that of packaging materials $12 per thousand cartons, and lithographed overwraps $4.50 per thousand. It is assumed that steam required for processing would be available from the parent plant at the rate of 75 cents per 1000 pounds of steam. Estimated manufacturing costs for 12-oz. cartons of frozen cooked rice are shown in Table 3.

TABLE 3

Estimated Cost of Manufacture for 12-oz. Carton of Frozen Cooked Rice

	Product per hour, lbs.		
	1500	4500	9000
Raw materials and packaging supplies	5.1c	5.1c	5.1c
Processing and packaging cost	1.1c	0.6c	0.5c
Transportation and casing	1.0c	0.9c	0.9c
Freezing and storage	1.2c	1.2c	1.2c
Indicated manufacturing cost	8.4c	7.8c	7.7c

If normal mark-ups for processor, broker, distributor, and retailer are added to the cost of manufacture, the indicated retail price of frozen cooked rice would be in the range of 13 to 15 cents per 12-oz. carton.

It is recognized that the cooking of rice on a commercial scale would vary somewhat from the laboratory procedure. The cooking time, for example, would need to be adjusted to allow for the longer period required to bring the raw rice to boiling temperature. The optimum rice loading on steaming belts has not been determined. The variations, however, should not result in any loss of quality of finished product.

LITERATURE CITED

1. Vinacke, W., Hartzler, E., and Tanada, Y. Processed Rice in Hawaii. Univ. Hawaii Agr. Expt. Station, *Tech. Bull.* 10 (1950).

An Exploratory Study of Respiration Rates of Microorganisms in Orange Juice as a Possible Index of Population

R. E. HENRY, N. H. STRODTZ, AND D. I. MURDOCK
Research Department, Continental Can Company, Inc., Chicago, Illinois

(Manuscript received January 25, 1951)

A rapid control method of estimating the microorganism population in orange juice with the aid of the polarograph in measuring oxygen consumption rates is suggested. Laboratory studies with pure yeast cultures in single-strength orange juice demonstrated the existence of a relationship between respiration rates and population. Limited field studies gave further indications of a relationship between oxygen consumption and microorganism population.

The present popularity of frozen orange juice concentrate is undoubtedly due to its excellent flavor characteristics, which in turn are related to the quality of the original fresh fruit used in its production. The maintenance of the high quality standards initially established by the citrus industry for this product is of such great importance that much thought and study is continuously being given to all phases of production and marketing which might affect the quality of the consumed product.

One of the factors which apparently is considered significant in the control of quality in the production of frozen citrus concentrate is the type and number of microorganisms present in the freshly pressed juice. At present, the microorganism content is estimated by conventional microbiological techniques which do not lend themselves to production control because two or three days are required for completion of the tests. Consequently, considerable interest has been expressed in better and more rapid methods which might be used for plant control.

The information reported here represents an attempt to adapt oxygen respiration measurements as a rapid means of estimating the microorganism population of orange juice.

EXPERIMENTAL

It first became necessary to devise a simple technique for measuring respiration or oxygen consumption rates in orange juice and, second, to select a test organism to evaluate this technique. In order to measure the rate of oxygen consumption, advantage was taken of the response of the dropping mercury electrode or polarograph* to oxygen dissolved in a suitable supporting electrolyte. Previous studies in this laboratory and by other investigators *(1, 2)* have shown that the oxygen content of orange juice and other fruit juices may be measured easily and accurately by this means.

Yeasts were selected for test purposes because it was assumed at the beginning of the study that yeast population would be a good index of the condition of the incoming fruit and the sanitation employed in the juice handling operations.

The nature of the polarographic curve or current-voltage curve for dissolved oxygen is such that the recording of the complete curve is not required for a determination. Therefore, the determination does not require an expensive recording instrument, but rather the simple charting of the galvanometer deflection at a fixed applied voltage, which in this instance was —0.4v. versus the saturated calomel electrode. This technique has been described by McKenzie and Lewis *(2)*. Therefore, an inexpensive simplified polarograph was constructed, a schematic diagram of which is shown in Figure 1. This instrument consisted of the usual type dropping mercury electrode, a saturated calomel reference cell, a galvanometer with a continuous type sensitivity control, and a manually controlled applied potential. The oxygen content expressed as percent saturation was plotted on semi-log paper against the time in hours.

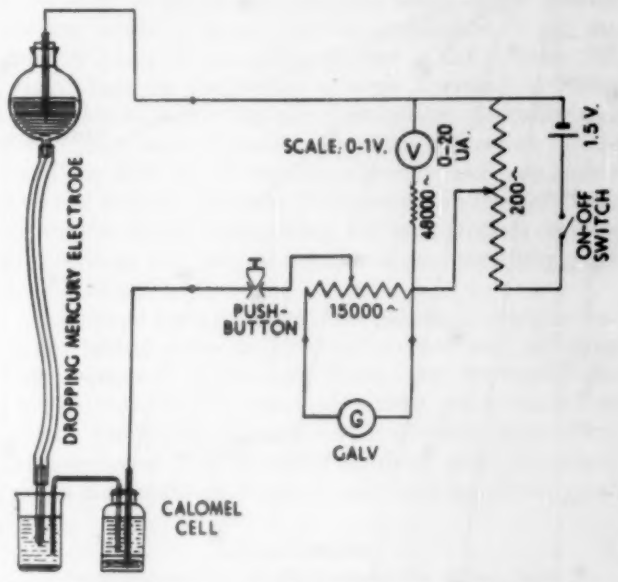


FIG. 1. Simple manual polarograph for dissolved oxygen determination.

In the past, our studies with sterile orange juice have shown oxygen consumption to take place at a rather slow rate which is specifically described by the equation for a first order reaction. A brief preliminary experiment with orange juice inoculated with a Tokay yeast at approximately one million cells per ml. showed the oxygen consumption to deviate quite significantly from the first order reaction of the uninoculated sterile sample. With this encouraging result, a program involving the study of oxygen utilization of three citrus yeast cultures in juice pressed from Florida oranges was outlined. In order to carry out this study, the following procedure was employed.

Freshly extracted orange juice was first pasteurized by heating rapidly to 76° C. (169° F.) followed by immediate cooling to incubation temperature which was 30° C. (86° F.) in this instance. Sixteen ounces of this orange juice in a 32-oz. bottle was then saturated with air by shaking vigorously for at least five minutes. Occasionally it was found necessary to filter the sample through cheese cloth when large particles or seeds interfered with the formation of the mercury drop at the dropping mercury electrode. The aerated juice was then transferred to two 8-ounce screw cap bottles, allowing approximately one inch of headspace to permit mixing. One sample was then inoculated with yeast cells, while the other served as a control.

* Instruments of this type are available commercially at several chemical supply houses.

In order to measure the oxygen content, both control and inoculated samples were taken from the 30° C. (86° F.) incubator, the cap removed, the dropping mercury electrode along with the reference cell bridge inserted in the orange juice, and the galvanometer deflection recorded. The screw cap was then replaced and the sample was returned to the constant temperature cabinet for further incubation. Residual currents were determined from deaerated samples and were found to be quite consistent.

Employing this procedure, the juice samples were inoculated with yeast cells at various levels in the range of 50,000 to 2,000,000 cells per ml. and plate counts made on acidified dextrose agar at the beginning and end of the experiment. Dissolved oxygen measurements were made at periodic intervals, and the resulting percent air saturation values plotted on semi-log paper versus time. A representative set of data is shown graphically in Figure 2.

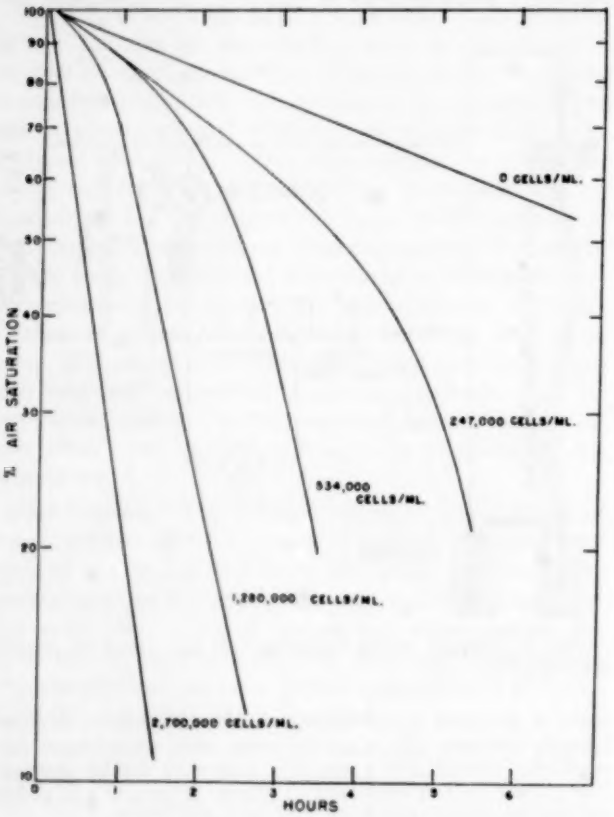


FIG. 2. Typical respiration rates of various concentrations of yeast cells in orange juice.

The calculation of comparative oxygen consumption values from data such as are shown in Figure 2 was difficult both because of the non-linearity of the curves and the wide range of rates. After a number of trials it was decided to make the time at which the rate was measured a function of the rate. This was accomplished in an arbitrary manner by drawing a straight line as shown in Figure 3 between 10% saturation at zero time and 100% saturation at six hours. The point at which a given curve intersected this line, then, was the time at which the oxygen absorption value was calculated. The net oxygen utilized by microbiological activity is the difference between the oxygen saturation of the blank (juice having no microbiological activity) and that of the sample, and is referred to hereafter as the "oxygen absorption index." Using this method of calculation the data found in Table 1 were assembled.

The graphical relationship indicated in Table 1 is shown in Figure 4. The extent to which the individual points scatter is no greater than would be expected from the normal error of plate counting.

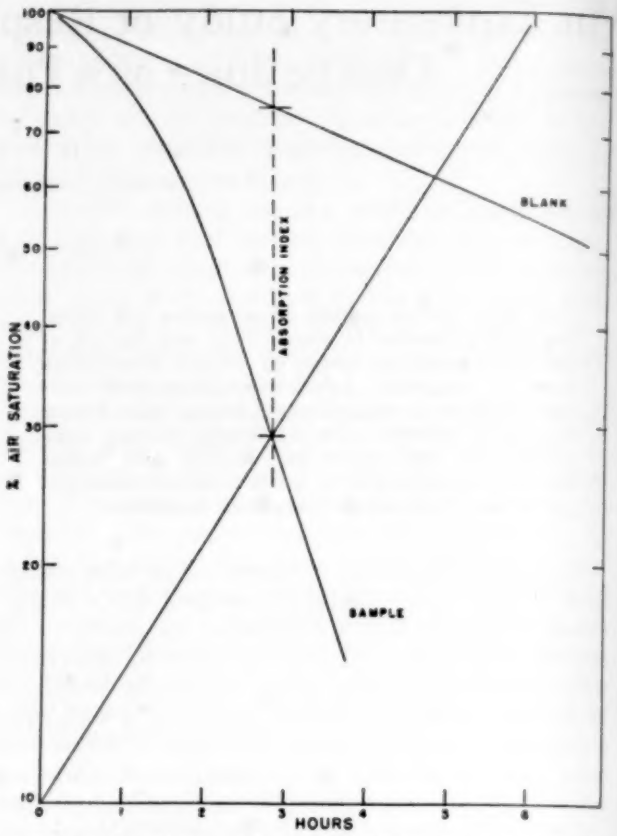


FIG. 3. Graphical method of calculating "oxygen absorption index."

The necessity of ascertaining whether the oxygen absorption value obtained was entirely due to microbial activity or in part to other interfering reactions instigated a search for a simple means of showing this distinction. Heating to 76° C. (169° F.) should inactivate yeast and other vegetative flora normally expected to be found in orange juice, but should not markedly affect enzymes. This method was tried and found to be satisfactory as shown by the data in Figure 5. In this instance, juice

TABLE 1

Oxygen Absorption Index and Plate Counts of Various Juices

Juice lot	Culture code	Oxygen absorption index	Plate count, on acidified dextrose agar, microorganisms/ml.
1	A	5.0	40,000
1	A	9.0	83,000
1	A	30.0	270,000
1	A	44.4	365,000
2	B	3.4	50,000
2	B	8.0	100,000
2	B	30.5	300,000
2	B	37.0	500,000
3	B	29.0	300,000
4	C	13.0	110,000
4	C	20.0	280,000
4	C	24.2	380,000
4	C	36.3	650,000
5	A	10.7	84,000
5	A	15.5	260,000
5	A	27.0	402,000
6	B	13.7	109,000
6	B	32.8	355,000
6	B	35.4	565,000
7	C	22.3	247,000
7	C	43.5	534,000
7	C	60.3	1,280,000
7	C	73.4	2,670,000

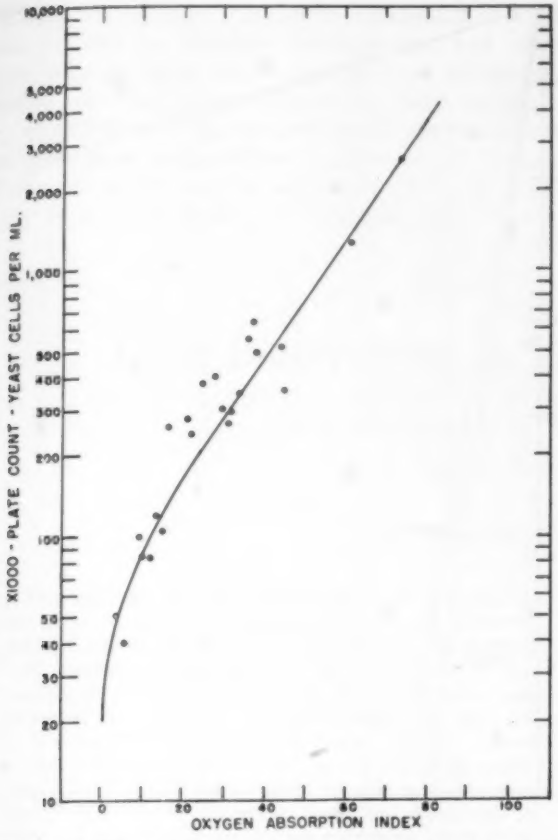


FIG. 4. Calibration of "oxygen absorption index" in terms of yeast cells per ml. of orange juice.

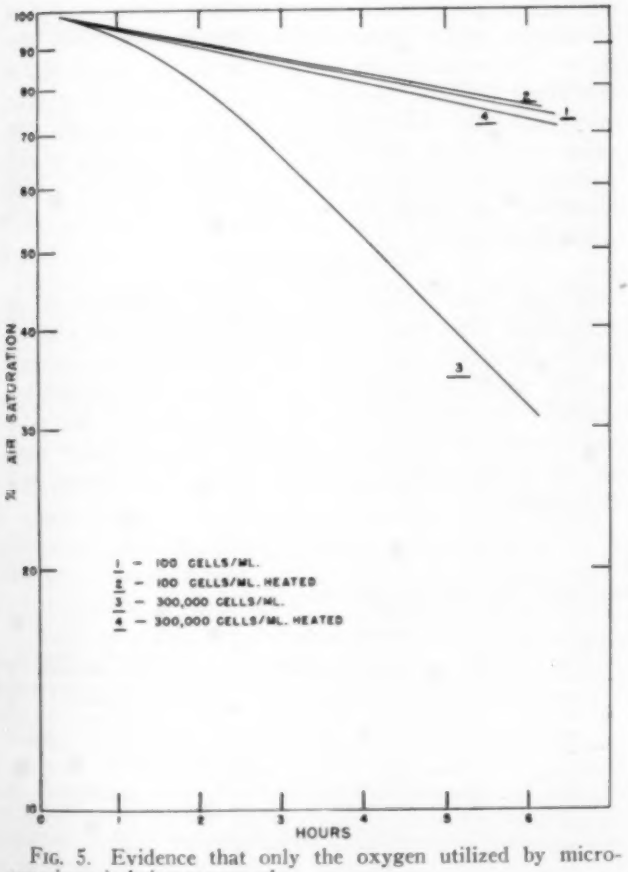


FIG. 5. Evidence that only the oxygen utilized by microorganisms is being measured.

containing 100 yeast cells/ml., an insignificant amount so far as polarographic data is concerned, was run, heated and unheated. The two curves obtained were practically identical. In a second experiment, a juice having a yeast inoculation of 300,000 cells/ml. consumed oxygen before pasteurization at significant rate, but after pasteurization the rate of oxygen consumption was almost identical with runs 1 and 2. This experiment was significant, not only because it demonstrated a method of blank preparation, but also because it furnished evidence that only the oxygen utilized by the microorganisms was being measured.

FIELD STUDIES

With the laboratory studies showing excellent possibilities of employing respiration or oxygen consumption rates as a means of evaluating the microbial content of orange juice, it was decided to attempt to study this technique in the field. As a consequence, a number of exploratory experiments were conducted in Florida at a plant producing frozen orange juice concentrate.

In order to obtain juice samples which might provide varying levels of microorganism population, it was decided to locate the sampling stations at the juice extractors. These, in this instance, were operated in banks of six to take care of the size distribution. Since the size distribution varies considerably, some extractors handle less juice than others and, consequently, build up higher levels of microorganisms. Plate counts in the past have shown the extractors handling the least amount of juice to contribute the greatest number of microorganisms per ml. of extracted juice.

A series of runs on juice from pineapple oranges was made, taking samples from extractors and finishing reels. Control samples or blanks to determine the oxygen consumption rates of orange juice, heated to destroy yeasts and bacteria, were obtained from three extractors and juice from the finishing reel. The blank results are found in Table 2, and because of the close

TABLE 2

Blank Determination of Microorganism-Free Orange Juice Collected at Different Points

Incubation time	No. 1 Extractor	No. 3 Extractor	No. 6 Extractor	Reel
(Initial air saturation)	100	100	100	100
1 hour	83	80	81	87
2 hours	69	69	70	73
3 hours	63	65	63	64
4 hours	57	59	58	58
5 hours	52	55	55	54
6 hours	49	51	51	51

agreement, juice from the finishing reels was used for subsequent blanks. A summary of all the extractor results is found in Table 3.

From these data there is an obvious disagreement between the plate count made on Lindegren's agar and the number of microorganisms as estimated with the polarograph based on the yeast calibration curve made in the laboratory studies. In examining the data further, it was observed that a better correlation existed between the visually estimated flow of fruit and polarographic count than that obtained from Lindegren's agar.

In an attempt to explain the lack of correlation obtained with Lindegren's agar, additional information concerning the possible effect of germicides in the wash water on plate counts and polarographic response seemed desirable. For this purpose oranges were taken

TABLE 3

Summary of Results Obtained with Juices from Different Extractors

Extractor	Flow of fruit	Oxygen absorption index	Polarographic count, micro-organisms/ml.	Plate count, on Lindegren's agar, micro-organisms/ml.
1	Rapid	5.5	57,000	10,000
2	Slow	25.9	240,000	6,000
3	Slow	38.2	420,000	7,000
4	Rapid	16.0	130,000	21,000
5	Slow	41.0	500,000	1,000
6	Very slow	56.2	1,100,000	2,000
1	Slow	10.0	88,000	121,000
2	Rapid	7.1	68,000	1,000
3	Rapid	10.1	89,000	6,500
4	Slow	10.8	91,000	10,500
5	Rapid	5.2	56,000	1,000
6	Slow	11.8	100,000	1,000
1	Very slow	42.2	520,000	484,000
2	Rapid	0.5	10,000	2,000
3	Rapid	3.4	44,000	———
4	Rapid	0.5	10,000	38,000 [b]
5	Slow	6.2	64,000	6,000
6	Rapid	1.6	33,000	2,000
1	Very slow	43.0	520,000	135,000
6	Slow	14.4	120,000	600
5	Very rapid	0.0	10,000	200
1	Slow	27.0	220,000	66,000
6	Rapid	0.0	10,000	300

[b] Aerobic spore-formers.

at various stages of treatment before extraction and hand pressed. A definite quantity of hand pressed juice from rotten oranges was added to the test sample to insure an easily measurable level of microorganisms. The results found in Table 4 show excellent agreement between the two methods of estimating microbial population.

Although these experiments have shown that the surface treatment of oranges did not interfere with the polarographic response or plate counts of hand extracted juice, the discrepancies found in the extractor studies remain unexplained.

Line samples of orange juice concentrate were also polarographed for use in comparison with samples of concentrate having distinct off-flavors proven to be of microbial origin but only showing moderately high plate counts. The off-flavored samples consumed oxygen at an extremely high rate, indicating a level of microbial contamination far in excess of that shown by the plate counts. In these instances the polarographic data apparently recorded microbial activity which was not detected by routine plate counting.

Further data relating to off-flavor and polarographic response is exhibited in Figure 6, which shows the curves obtained by hand pressing normal oranges,

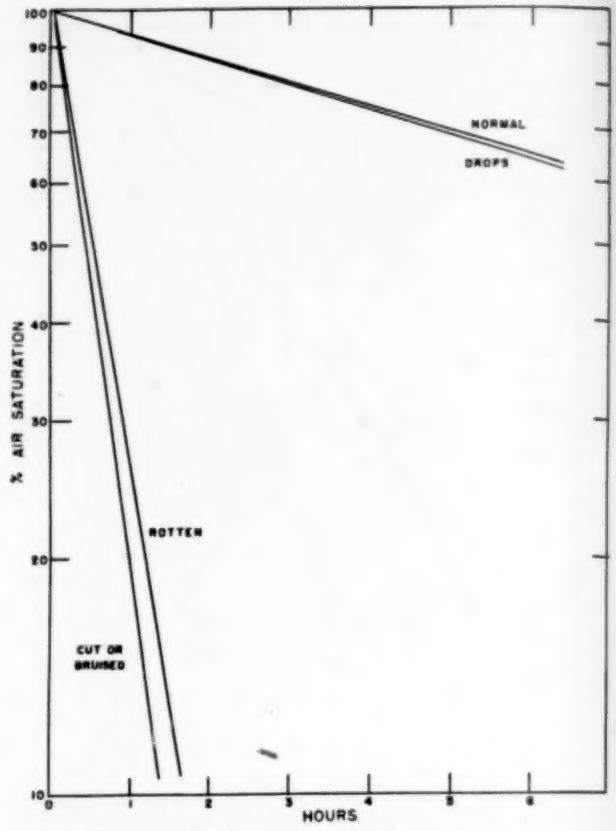


FIG. 6. Relation of defective fruit and polarographic response.

drops, rotten, and mechanically damaged fruit. The latter three groups were found to have various types of off-flavors which were easily distinguished from the flavor of normal orange juice. The drops, whose flavor difference probably resulted from chemical rather than microbiological abnormality, showed essentially the same response as the normal; while the others, which were proven by plate counting to contain extremely high levels of microorganism content, showed very rapid respiration rates.

SUMMARY

It has been shown that oxygen consumption or respiration rates may be conveniently measured with an inexpensive and easily operated instrument, in contrast to the usual elaborate set-up required for respiration studies. In addition, the laboratory studies with pure yeast cultures in single strength orange juice have shown a correlation between respiration rates and population.

TABLE 4

Comparison of Polarographic Counts with Plate Counts from Hand-Extracted Juice

Code	Source	Extractor	Oxygen absorption index	Polarographic count, microorganisms/ml.	Plate count, on Lindegren's agar, microorganisms/ml.
1M	Truck (hand-washed)	Hand	52	880,000	880,000
2M	After first chlorine spray	"	54	960,000	790,000
3M	After borax and bin storage	"	18	150,000	160,000
4M	After final chlorine wash	"	30	300,000	520,000
1M	Truck (hand-washed)	Hand	35	370,000	325,000
2M	After first chlorine spray	"	44	580,000	490,000
3M	After borax and bin storage	"	44	580,000	630,000
4M	After final chlorine wash	"	44	580,000	460,000
5M	Juice from extractor	From line	57	1,100,000	610,000

In the field studies there were indications of a relationship between oxygen consumption and microorganism population, and in one instance, off-flavors of possible microbial origin. However, these studies are only exploratory in nature and much additional information must be accumulated in order to fully evaluate the use of respiration rates as measured by the polarograph as a rapid means of estimating the microbial population of orange juice and other products to which it might apply.

LITERATURE CITED

1. Lewis, V. M., and McKenzie, H. A. Amperometric determination of dissolved oxygen in orange juice. *Anal. Chem.*, **19**, 643 (1947).
2. Lindquist, J. R. Rapid dissolved oxygen test for fresh citrus juices. *Food Inds.*, **19**, 182 (1947).

Heat Inactivation of Polyphenolase in Fruit Purees

K. P. DIMICK, J. D. PONTING, and B. MAKOWER
Western Regional Research Laboratory,[a] Albany, California

(Manuscript received December 29, 1950)

Thermal inactivation characteristics of polyphenolase were investigated in purees of apples, apricots, peaches, pears, and grapes to determine conditions for heat treatments required for the prevention of enzymatic browning. The amount of inactivation was measured as a function of time, temperature, and pH in a continuous-flow apparatus which allowed a part of the reaction to be studied under isothermal conditions. The rate of inactivation at constant temperature was different for each fruit and appeared to follow a logarithmic law. The enzyme in each fruit was found to have a characteristic pH of maximum thermal stability. These data permitted the estimation of conditions, times, and temperatures required for essentially complete enzyme inactivation in the different fruit purees.

One of the requirements for the preparation of stable fruit purees is the inactivation of those natural enzymes which catalyze certain deteriorative reactions. The enzyme polyphenolase (polyphenol oxidase) is considered especially important in that respect, because it promotes oxidation which results in browning, alteration of flavor, and loss of ascorbic acid *(11)*.

Enzyme destruction is readily accomplished by heat treatment. Although considerable work has been reported on the thermal inactivation of enzymes in various fruit products *(7, 4, 8, 9, 3, 1, 10)*, very little information exists on the exact time-temperature relationship for inactivation of polyphenolase in purees of specific fruits. The objective in the work reported here has been to obtain data for several fruits that would define, with as much precision as possible, conditions for practical operations, particularly in flash-heating procedures.

Recent developments *(2, 6)* have shown that improved quality is obtained when the heat treatment is conducted at a high temperature for a short time. For that reason an effort was made in the present investigation to obtain data in, or close to, the high temperature region that might be used in practical flash-heating operations.

Measurement of the rate of inactivation at high temperatures (80°-100° C.) cannot be accomplished by the conventional methods *(9, 3)* of heating samples for various times in a constant-temperature bath and analyzing for residual enzyme contents. The inactivation reaction would be nearly completed during the relatively long preheating period necessary to reach the desired temperature, and it would thus be impossible to measure any changes under isothermal conditions. To obviate this difficulty a flow method was employed wherein the preheating time and subsequent cooling to quench the reaction were relatively short. The purees were pumped continuously through a steam-heated tube (preheated) to bring them to a desired temperature, then through heat-insulated tubes of various sizes to provide holding times at the desired temperature, and finally through a rapid cooler to stop the inactivation reaction. The results obtained with such a system are of particular interest because the flow method is commonly used for commercial heat treatment of fluid foods. The extent of the overall reaction was determined from measurements of enzyme activities before they were heat treated and after cooling. For the isothermal portion of the reaction, the initial activity was that of the puree immediately after it had been preheated; the final activity was that of the cooled puree.

Measurements were made on purees of Royal apricot, Elberta peach, Gravenstein apples, Bartlett pear, and Concord grape. The effects of pH, time, and temperature were studied. The effect of each variable was determined with other variables held constant.

EXPERIMENTAL

Apparatus. The apparatus used for heat treating the purees is illustrated diagrammatically in Figure 1. A holding vessel (a) and a small stainless-steel gear metering pump (b) provided the means for continuously pumping the puree through the system. The heating section (c) consisted of a steam-heated 9-foot section of ¼-inch (20-gauge) stainless-steel tubing. A

[a] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. A preliminary report on the work discussed in this article was presented before the Northern California Section of IFT in December, 1948, at the Western Regional Research Laboratory.

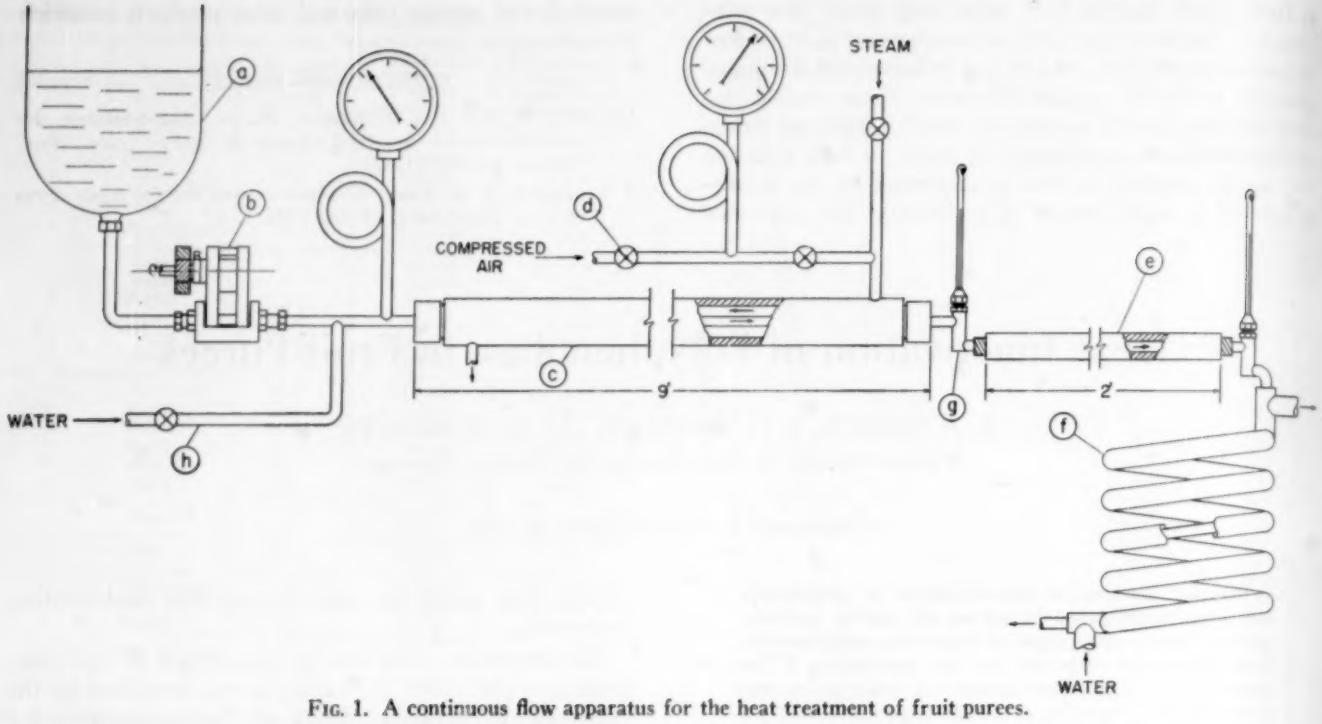


FIG. 1. A continuous flow apparatus for the heat treatment of fruit purees.

mixture of steam and compressed air was admitted to the jacket in a direction counter to the flow of puree. By manual regulation of the amount of compressed air with a regulating valve (d), the temperature of the puree emerging from the heating section could be controlled to within $\pm 0.2°$ C. Heat-insulated tubes (e) (holding sections) placed immediately after the heating section provided a means for holding the puree at the desired temperature for a definite time. The puree was then quickly cooled by passage into a cooling coil (f) or by being caught directly in a weighed amount of crushed ice. It was established that the puree was cooled to a temperature at which rate of inactivation became negligibly slow in less than 0.5 second by either method. A water inlet (h) is provided to wash out the system after each run.

All measurements were made with the metering pump set to deliver 420 ml. of puree per minute. At this rate, seven seconds were required for the puree to flow through the heating section. This time, plus any additional time required for the puree to reach the cooling section, is defined as the processing time. The minimum processing time, therefore, was eight seconds, since one second was required for the puree to flow through the thermometer well and outlet tube.

The duration of the isothermal part of the reaction was determined from the time required for the puree to flow through a holding section. The holding sections consisted of interchangeable insulated glass tubes about 50 cm. long. They varied in inside diameter from 5.2 to 30 mm. and permitted a variation in the holding time of about 1 to 53 seconds. The processing time, however, could be varied about 8 to 60 seconds because of the additional 7 seconds necessary for the puree to pass through the preheater.

The measurement of the isothermal rate involves knowledge of the reaction time which, as explained above, was calculated from the rate of flow and the dimensions of the holding tubes. This calculation involves an assumption that the rate of flow was the same for all parts of the puree (along the entire cross section of the holding tube). A requirement for this condition is that the flow be turbulent rather than streamlined.

Though there is no direct evidence on the extent of turbulence in the holding tubes, the following arguments may be offered in support of the above assumption: First, turbulence was undoubtedly produced when the puree passed through the Z-shaped thermometer well (g in Figure 1) and entered the holding tube and thus turbulent flow must have existed at least along part of the holding tube. Second, self-consistent results were obtained in the measurements, as shown by the fact that the rate could be expressed in terms of a logarithmic law. Inconsistent results were obtained, however, when an attempt was made to use a 50-mm.-diameter tube, which is larger than any used in this investigation. It is concluded, therefore, that with the holding tubes actually used, the errors due to insufficient turbulence were probably of no great importance.

Enzyme Activity Measurement. The activity of the polyphenolase in the fruit preparation was determined according to a method described by Ponting and Joslyn *(12)*. Catechol is darkened very rapidly by this enzyme, and the rate of its darkening forms the basis of the activity measurement. A blend of 50 g. of puree was made in 150 ml. of ice water and the mixture filtered through coarse paper. The rate of color formation was measured with a Coleman photoelectric colorimeter at 420 millimicrons on an aliquot of the filtered extract, diluted to a standardized volume with buffered 0.05 *M* catechol solution at pH 5. Enzyme activity is expressed as change in optical density/ml. of extract/minute.

Preparation of purees. The purees were prepared from fresh fruit by the use of a screw-feed pulper, with a screen having holes 0.033 inch in diameter. With the peaches, apricots, and grapes used in these experiments, browning was not rapid; about 25 pounds of the puree could therefore be prepared at once and held in an ice bath for one to two hours. At intervals, two-pound samples of the puree were removed and heat treated. With apples and pears it was found that browning, with consequent reduction of the polyphenolase activity, occurred so rapidly that this procedure could not be used. Therefore, an individual sample of the puree (approximately two pounds) was prepared from randomly sampled fresh fruit for each run at one holding time and temperature. The time required to puree the fruit and to heat-treat the sample was approximately three minutes.

RESULTS

The rate of decrease of polyphenolase activity at constant temperature appears to follow a logarithmic law as shown by linear relations obtained in plotting the

logarithm of residual enzyme activity against time. An example of such plots is given in Figure 2, which shows the results obtained with purees of Bartlett pears at various temperatures.

Although the plots encompass only the isothermal part of the inactivation process, the percent of inactivation at any given processing time represents the change that occurred during the seven-second non-isothermal preheating period, plus the isothermal change during the remainder of the time. It is evident from these plots that considerable inactivation occurred in the preheater. An inspection of Figure 2 shows that if the lines were extrapolated to zero time, most of them would intersect the ordinate below the original 100% activity,

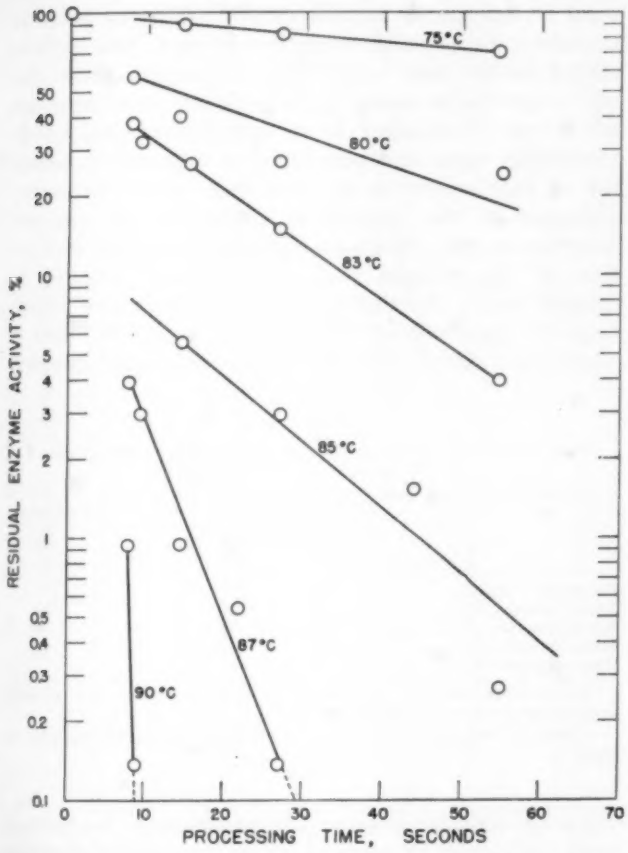


FIG. 2. Course of inactivation of polyphenolase in pear puree at various temperatures.

showing that even more inactivation had occurred in the preheater than would be expected from the rate law for the isothermal region. A probable explanation of this occurrence is that a portion of the puree, near the periphery of the preheater tube, became superheated and resulted in an overall greater inactivation than might be expected from the average lower temperature of the whole puree stream. At the lowest temperature, 75° C., this effect was apparently negligible. A uniform temperature would, however, be expected in the holding tubes owing to the mixing and turbulence that undoubtedly occurred in the Z-shaped thermometer well between the preheater and the holding tube.

From the data for pears in Figure 2 and from similar smoothed plots for other fruits, the results obtained for the inactivation of polyphenolase at different temperatures and processing times are summarized in Table 1. The table includes the measured values of the original pH and the original enzyme activity of the puree. It should be noted that some of the figures for inactivation in Table 1 represent enzyme activities of less than 0.001 unit, which is approximately the lower limit for enzyme determination by the method used *(12)*. These figures, shown in italics, were obtained by extrapolation of the logarithmic plots (as in Figure 2) to longer processing times on the assumption that the same logarithmic relationship held for the lower activities. The symbol $<0.1\%$ means that the residual enzyme activity was less than 0.1% of the original. This amount was generally not directly measurable.

TABLE 1

Effect of Time and Temperature on the Inactivation of Polyphenolase in Various Fruit Purees

Kind of fruit	pH of unheated puree	Temp., °C.	Percent enzyme remaining [b] at indicated processing times [c] seconds					
			8	10	15	20	40	60
Royal apricots	4.0	75	61	47	39	34	23	16
		83	25	14	3	0.5	*<0.1*	....
		92	0.3	*<0.1*	....	....	....	....
Elberta peaches	3.5	70	59	52	35	24	9	6
		75	24	16	5	2	*<0.1*	....
Gravenstein apples	3.1	65	40	37	32	28	15	8
		70	32	22	7	5	2	1
		73	1.2	1.0	0.7	0.5	0.1	*<0.1*
		75	1.2	0.9	0.4	0.2	*<0.1*	....
		80	0.2	*<0.1*	....	....	....	....
Bartlett pears	3.9	75	95	94	91	89	78	68
		80	66	55	41	36	26	13
		83	41	32	26	20	8	3
		85	31	19	6	4	3	0.3
		87	4	3	1	0.5	*<0.1*	....
		90	1	*0.1*	*<0.1*	....	....	....
Concord grapes	3.3	65	74	69	64	60	50	40
		75	59	53	39	29	8	3
		77	37	29	16	8	*<0.1*	....
		80	16	9	3	*<0.1*	....	....

[b] Data taken from smoothed curves. The first 7 seconds of the processing time is the preheating period. During this time the reaction is not isothermal. Figures in italics obtained by extrapolation.

[c] Original enzyme activity is expressed as rate of color development in a standard catechol solution. The activity units are: change of optical density per ml. of extract per minute. Original activities were 0.44, 0.27, 1.80, 0.74, and 0.62 for apricots, peaches, apples, pears, and grapes, respectively.

Rates of heat inactivation of the different fruit purees during the isothermal period varied widely. A comparison can be made most readily for the reaction at 75° C. because data for this temperature are available in Table 1 for all fruits. From the slopes of the semilogarithmic plots it was calculated that the times in seconds required to reduce the activity to one-tenth of its former value were as follows: pear, 390; apricot, 80; grape, 27; peach, 12; and apple, 7.5. Thus the rate of inactivation at 75° C. was most rapid in apple and slowest in pear puree.

It must be pointed out, however, that this order may not necessarily be true at another temperature, because

the temperature coefficients for the different fruits are quite different. Though the available data do not permit accurate determination of temperature coefficients, the following estimates have been made for E, the energy of activation in kilocalories, and for Q_{10}, the ratio of rates for a 10° C. rise in temperature: pears, $E = 100$, $Q_{10} = 60$ (75°-85° C.); apricots, $E = 79$, $Q_{10} = 25$ (75°-85° C.); grapes, $E = 66$, $Q_{10} = 16$ (70°-80° C.); apples, $E = 83$, $Q_{10} = 39$ (65°-75° C.); peaches, $E = 117$, $Q_{10} = 120$ (70°-80° C.). These values are very high when compared with those for ordinary chemical reactions but they are of the same order of magnitude as previously found for heat denaturation of other enzymes or proteins *(13)*.

It is evident from these high values of the temperature coefficient that great care must be exercised in controlling the temperature of the inactivation process to insure that the desired degree of inactivation has been reached. This is illustrated in Figure 3, which shows the experimental results for residual enzyme activity in

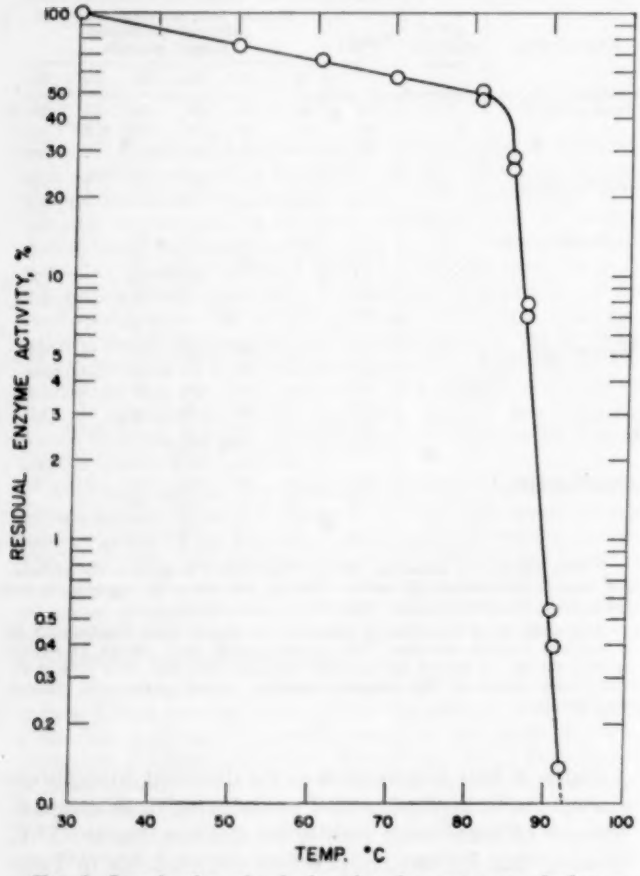


FIG. 3. Inactivation of polyphenolase in pear puree during an 8-second processing treatment at various temperatures.

pear puree as a function of holding temperature for a constant, eight-second processing time. From 30° to about 80° C., a 50-degree increase in temperature results in a two-fold change in activity (from 100 to about 50%); a further increase of about 12° C. (from 80° to 92° C.), however, results in approximately 500-fold change in residual activity (from 50 to 0.1%). This temperature region is characterized in Figure 2 by the approximately linear and very steep portion of the curve. If 92° C. is arbitrarily taken as the temperature for essentially complete enzyme inactivation (residual activity 0.1%), then it is apparent from the curve that a lowering of only a few degrees in temperature will cause an appreciable amount of enzyme to remain in the puree and may result in undesirable browning of the puree in subsequent storage.

The relation between browning tendency (or rate), and the residual enzyme activity has not been determined in this study and will require further investigations. As shown by Guadagni, Sorber, and Wilbur *(5)*, the browning rate of fruit is a function of enzyme activity, substrate concentrations, and other factors which must be determined experimentally. It is not possible, therefore, to establish from the present data definite conditions for heat inactivation of polyphenolase that will insure no browning of the fruit purees under given conditions of storage. It is only possible to specify processing times and temperatures required to reduce the enzyme activity to an arbitrarily chosen low value. (Because of the logarithmic nature of the enzyme-inactivation rate shown in Figure 2, complete destruction of the enzyme would theoretically require an infinite time.) A tabulation of such processing conditions for reduction of enzyme activity to 0.001 unit is shown in Table 2. This activity level is approximately

TABLE 2

Time-Temperature Relations for Essentially Complete Inactivation [a] of Polyphenolase in Various Fruits [b]

	Temperatures (° C.) at the indicated times			
	9 sec.	24 sec.	60 sec.	120 sec.
Gravenstein apples	81	75	73	70
Bartlett pears	91	88	86	84
Elberta peaches	82	76	75	72
Royal apricots	92	....	83	....
Concord grapes	82	80	....	....

[a] Essentially complete inactivation is taken to mean that residual enzyme activity is 0.001 activity unit.

[b] Data in this table are estimates based on measurements recorded in Table 1.

the lower limit for enzyme determination by the method used *(12)*, and is referred to as essentially complete inactivation. Inactivation temperatures are given for several processing times for each fruit. The data in Table 1 were obtained from logarithmic plots (as in Figure 2). Holding times at the indicated temperatures can be obtained by subtracting seven seconds (preheating time) from the given processing times.

It can be noted from Table 2 that the processing conditions are quite different for the various fruits. Processing temperatures may differ as much as 12° C., as in the case of apples and apricots, for a 9-second processing time. The differences may be caused by many factors such as concentration of the enzyme, temperature coefficient, ionic strength, pH, and undoubtedly others.

The effect of varying the pH of a particular fruit puree was also investigated. The pH was adjusted be-

fore heat treatments by the addition of 6 *N* sodium hydroxide or hydrochloric acid. It was found that for each fruit there is a certain pH at which polyphenolase is most stable toward heat. At higher or lower pH values the stability decreases markedly (rate of inactivation increases). The effect of varying the pH of pear puree on the degree of inactivation at constant processing time and temperature is shown in Figure 4. It is seen that at the pH of maximum stability, 6.0, very little, if any, of the enzyme has been inactivated, whereas nearly complete inactivation occurred at a pH greater than about 10 or less than about 2. With other fruits the pH of maximum stability was found to be as follows: apricots, 3.9; apples, 6.2; grapes, 4.5. Detailed results taken from curves similar to Figure 4 are given in Table 3. Comparison with the natural pH values of the fresh purees (Table 1) shows that only with the apricots did the pH of maximum stability nearly coincide with that of the fresh fruit. It is also interesting to note that heat treatment caused a decrease of about 0.5 pH unit with the apricot puree but produced practically no change with the other fruits that were investigated.

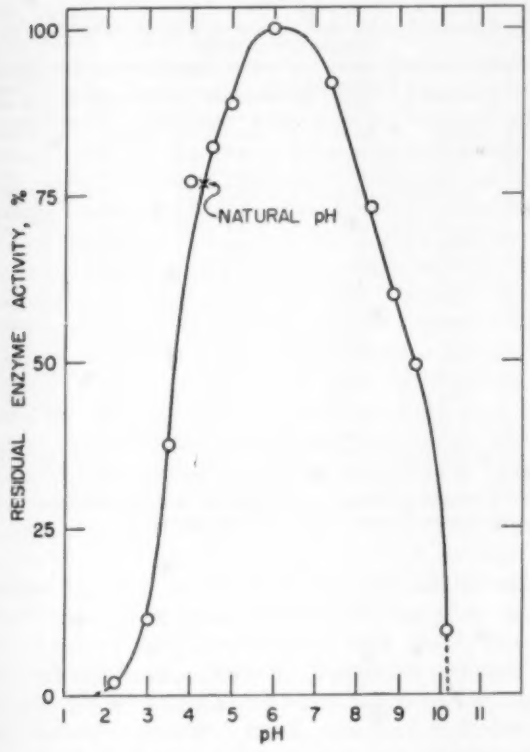


FIG. 4. Effect of pH on thermal stability of polyphenolase in pear puree at constant processing time (8 seconds) and temperature (78° C.).

TABLE 3

Effect of pH on Thermal Stability of Fruit Polyphenolase at Constant Processing Time and Temperature

Fruit	Remaining enzyme activity in percent at various pH values								
	pH of puree								
	2	3	4	5	6	7	8	9	10
Gravenstein apples Time: 10 sec. Temp.: 73° C.	<0.3	2	11	37	44	45	39	28	10
Bartlett pears Time: 8 sec. Temp.: 78° C.	1.0	12	68	89	100	96	78	57	27
Concord grapes Time: 8 sec. Temp.: 77° C.	<0.8	2	28	37	32	26	19	12	....
Royal apricots Time: 10 sec. Temp.: 74° C.	<0.3	0.7	71	57[1]	....	....	....	....	....

[1] pH value = 4.4.

CONCLUSIONS

Because of the differences in the composition of different varieties of fruits or of the same varieties grown under different agronomic or climate conditions, one would not expect that the data obtained on the fruits used in this investigation will be quantitatively applicable to fruits from other sources. The information obtained should serve, however, as a useful guide in establishing practical procedures for heat inactivation of polyphenolase in the kinds of fruits investigated.

From this information it is possible to estimate the conditions (time and temperature) of heat treatment to reduce the polyphenolase activity to a certain desired value. Table 2 gives such conditions for a particular residual activity, 0.001 unit. This, however, is merely an arbitrarily selected value and further research is needed to determine how much activity may be left to insure that no appreciable browning will result under particular storage conditions.

The selection of the proper conditions for heat treatment involves other important considerations, especially the organoleptic quality of the resulting fruit puree. Accurate data on this subject are also meager. Investigations have therefore been initiated at this Laboratory on several fruit purees to determine the relation between rate of browning and residual enzyme activity under certain storage conditions and to establish the relation between organoleptic quality and temperature of heat treatment.

LITERATURE CITED

1. ALVEREZ, A. S. Conservación del jugo de naranja por los procedimientos de pasteurización y "flash pasteurización." *Rev. ind. y agr. Tucumán*, **29**, 247 (1939).
2. Anon. New process in canning orange juice. *Food Packer*, **28** (12), 42 (1947).
3. AXELROD, B. Phosphatase activity as an index of pasteurization in citrus juices. *Fruit. Products J.*, **26**, 132 (1947).
4. FONG, W. Y., AND CRUESS, W. V. The effect of pH on the inactivation temperature of fruit oxidase. *Plant Physiol.*, **4**, 537 (1929).
5. GUADAGNI, D. G., SORBER, D. G., AND WILBUR, J. S. Enzymatic oxidation of phenolic compounds in frozen peaches. *Food Technol.*, **3**, 359 (1949).
6. HEID, J. L. Concentrating citrus juices by the vacuum method. *Food Inds.*, **15** (5), 62 (1943).
7. JOSLYN, M. A., AND MARSH, G. L. Some factors involved in the preservation of orange juice by canning. *Fruit Prod. J.*, **14**, 45 (1934).
8. KAPLAN, A. M., ESSELEN, W. B., AND FELLERS, C. R. Enzyme systems of canned acid foods. *Ind. Eng. Chem.*, **41**, 2017 (1948).
9. KERTESZ, Z. I. Pectic enzymes. III. Heat inactivation of tomato pectinmethoxylase (pectase). *Food Research*, **4**, 113 (1939).
10. MARSHALL, R. E., AND KREMER, J. C. Sterilization of apple juice by flash pasteurization. Mich. Agr. Exp. Sta. Quar. *Bull.*, **20**, 28 (1937).
11. MARSHALL, R. E., AND KREMER, J. C. Further studies on preservation of apple juice by flash pasteurization. Mich. Agr. Exp. Sta. Quar. *Bull.*, **21**, 12 (1938).
12. PONTING, J. D., AND JOSLYN, M. A. Ascorbic acid oxidation and browning in apple tissue extracts. *Arch. Biochem.*, **19**, 47 (1948).
13. SUMNER, J. B., AND SOMERS, F. G. Chemistry and Methods of Enzymes, 2nd Ed., 1947. Academic Press, Inc., N. Y.

Reduced Ascorbic Acid Content of Milk at Different Stages of Processing[a]

ARTHUR D. HOLMES

Massachusetts Agricultural Experiment Station, Amherst, Massachusetts

(Manuscript received October 24, 1950)

Samples of milk taken at different intervals in the pasteurization and bottling process show significantly different amounts of reduced ascorbic acid. These differences may be due to atmospheric oxygen or to contact of the milk with the processing equipment.

Milk as it is drawn from the cow ordinarily contains 20-25 mg. reduced ascorbic acid per liter. If milk could be consumed at this stage, it would contribute materially to the daily requirements of the average person for this essential vitamin. Unfortunately, before commercial retail milk reaches the ultimate consumer, it loses a large proportion of its original reduced ascorbic acid. This loss occurs during pasteurization, distribution, and storage in the home refrigerator. About one-fifth of the original reduced ascorbic acid in milk is lost during pasteurization by the holding method. Reedman *(10)* found that milk pasteurized by this method lost 25% of its original vitamin C; Woessner, Weckel, and Schuette *(17)*, Elvehjem *(2)*, and Mawson and Kon *(8)* observed a 20% loss; and Holmes, Tripp, Woelffer, and Satterfield *(4)* reported an 18.7% loss. During studies in this laboratory of the loss of reduced ascorbic acid from milk pasteurized by the holding process, it was noted that different bottles of milk from the same lot of pasteurized milk did not contain the same amount of reduced ascorbic acid; and this study was undertaken to determine the cause of that variation.

EXPERIMENTAL

In order that the milk studied should be representative of milk consumed during the college year, samples were taken between August 1 and May 1 from seventeen lots of milk processed by the Dairy Industry Department. The milk was pasteurized in a covered, 850-quart, stainless steel vat equipped with stainless steel paddles for agitating the milk during pasteurization for thirty minutes at 61.5° C. (143° F.). Since the head-room space above the milk soon became filled with vapor, very little atmospheric oxygen came in contact with the milk. As soon as pasteurization was completed, the milk was passed through nickel alloy metal pipes, a brass pump, over a covered tinned-copper surface cooler to the bottle filler, which was equipped with a stainless steel bowl.

Four samples were taken from each lot of milk; i.e., the first sample was representative of the thoroughly mixed cold milk in the pasteurizing vat before heating; the second sample, hot milk, was taken from the vat as soon as pasteurization was completed; the third sample was from the first twenty quarts of milk passed through the cooling and bottling equipment; and the fourth sample was the last milk through that system. The samples were taken at once to the laboratory and within an hour assayed for reduced ascorbic acid by the Sharp *(12)* method as modified by Holmes *(6)*.

[a] Contribution No. 777, Massachusetts Agricultural Experiment Station.

RESULTS AND DISCUSSION

The individual values obtained from the 68 samples of milk assayed for reduced ascorbic acid are reported in Table 1. The raw milk samples varied from 17.3 mg. per liter to 20.8 mg. and averaged 18.6 mg. of reduced ascorbic acid per liter. This value is in accord with values of 18-21 mg. by Sherman and Lanford *(15)*, 17.4 mg. by Woessner, Weckel, and Schuette *(18)*, 25 mg. by Kothavalla and Gill *(7)*, and 18 mg. per liter reported by Holmes, Jones, Wertz, Esselen, and McKey *(5)*.

TABLE 1

Reduced Ascorbic Acid Content of Milk at Different Stages of Processing

Sample no.	Raw milk	Pasteurized milk	First milk [b]	Last milk [c]	Volume of milk
	mg./l.	*mg./l.*	*mg./l.*	*mg./l.*	*quarts*
1	18.3	16.8	8.4	15.2	400
2	17.5	17.0	4.1	14.4	400
3	17.8	16.2	4.7	15.2	800
4	19.1	17.5	4.1	16.0	800
5	17.5	17.5	4.1	13.9	560
6	19.5	17.4	3.6	15.4	840
7	18.5	18.0	4.2	14.8	840
8	17.3	16.2	5.8	14.7	825
9	18.3	18.3	7.9	15.2	840
10	19.4	17.8	5.2	17.3	840
11	18.7	16.6	8.8	16.6	835
12	17.8	14.7	5.2	13.1	820
13	17.4	16.4	5.3	14.7	840
14	20.8	19.2	7.7	19.2	840
15	19.9	16.8	7.9	16.2	820
16	20.8	19.5	6.3	19.5	.....
17	17.4	14.8	7.4	13.2	840
Average	18.6	17.1	5.9	15.6	.....

[b] First milk passed through the cooling and bottling equipment. [c] Last milk passed through the cooling and bottling equipment.

The ascorbic acid content of the pasteurized milk at the conclusion of the thirty minutes' heating at 61.5° C. (143° F.) ranged from 14.7 to 19.5 mg. per liter and averaged 17.1 mg. This average loss of 1.4 mg. per liter indicates that the milk retained over 92% of the reduced ascorbic acid that it contained at the beginning of pasteurization, and at the conclusion of pasteurization it was relatively rich in reduced ascorbic acid. However, this result is not applicable to a human dietary consideration of the nutritive value of milk, for the ultimate consumer cannot immediately use milk at the conclusion of processing.

The results obtained for seventeen samples of the first milk through the pipe lines supplying the surface cooler and bottle-filler ranged from 3.6 mg. per liter to 8.8 mg., with an average of 5.9 mg. of reduced ascorbic acid per liter. Thus it averaged a loss of 11.2 mg. per liter, or over 65% of the reduced ascorbic acid that it contained at the conclusion of pasteurization.

One factor that probably affected this loss was atmospheric oxygen. When the heated milk passed through the equipment in its progress from the pasteurizing vat to its final glass bottle market package, it came in contact with the atmosphere that filled the equipment, but after the pipe lines and the cooling and bottle-filling equipment were thoroughly flushed out with milk, the loss of reduced ascorbic acid dropped to 8.8 percent for the last milk through the equipment.

A second factor that may have affected the excessive loss of reduced ascorbic acid was the contact of the first milk with the processing squipment. Woessner, Weckel, and Schuette *(18)* pasteurized milk in equipment that included partially worn tinned-copper piping that introduced 0.21 p.p.m. of copper into the milk, and it caused the destruction of as much as 35.6% of the ascorbic acid. Stull, Herreid, and Tracy *(16)* reported that milk which contained 0.3 p.p.m. of added copper lost 56.3% of its reduced ascorbic acid during pasteurization. Sharp, Trout, and Guthrie *(13)* state that milk which came in contact with exposed copper and the copper alloy of the bottle-filler acquired copper and that pasteurization as ordinarily carried out by the average distributor has an adverse effect on the ascorbic acid of the milk. Sharp and Hand *(14)* reported that the ascorbic acid in oxygen-free milk is resistant to heat and dissolved copper, but if milk contains dissolved oxygen, then processes which involve exposure to copper or copper alloys tend to accelerate the destruction of reduced ascorbic acid. Reif and Schormüller *(11)* tested the effect of four types of stainless steel on the reduced ascorbic acid content of milk. The chromium-nickel and the chromium steel were without effect. A steel containing 8% manganese had a strong oxidizing effect, and a titanium steel had a very pronounced effect. Kothavalla and Gill *(7)* found the least destruction of reduced ascorbic acid occurred when milk was pasteurized in a vessel lined with nickel and the greatest destruction when naked copper was used. Pratt *(9)* reported that milk pasteurized in an open nickel vessel exposed to air contained 15 p.p.m. of nickel, but the nickel did not increase the destruction of the reduced ascorbic acid in the milk; and Woessner, Elvehjem, and Schuette *(18)* state that evaporated milks manufactured in copper equipment may contain more reduced ascorbic acid than milks manufactured in stainless steel equipment. The reader who may wish to consider, in greater detail, the possible action of copper upon milk is referred to a paper by Brown and Thurston *(1)*, 412 references, and a paper by Greenbank *(3)* with 231 references.

The amount of reduced ascorbic acid in samples of the last milk through the cooling and bottling system varied from 13.1 mg. per liter to 19.5 mg., and averaged 15.6 mg. per liter. Thus the last milk through the equipment retained over 91% of the reduced ascorbic acid that it contained when pasteurization was completed. The total loss of reduced ascorbic acid for the last milk to pass through the pasteurizing equipment, 15.1%, is appreciably less than the pasteurization losses of 20% or more reported in the literature. The average values of 5.9 mg. of reduced ascorbic acid per liter for the first milk and 15.6 mg. for the last milk through the equipment show the extent to which the ascorbic acid content of pasteurized milk may vary even when two bottles are taken promptly from the same lot of pasteurized milk. These values show one cause of the wide variation in the reduced ascorbic acid content of commercial retail milk even though samples are taken from a single day's production of a typical dairy.

SUMMARY

A study was made of the reduced ascorbic acid content of milk at different stages of processing. Four samples of milk were collected at each of seventeen intervals during the period from August 1 to May 1; i.e., one sample was taken from the thoroughly mixed cold milk in the vat before pasteurization was started; one from the same milk when pasteurization was completed; one from the first milk to pass through the cooling and bottle-filling equipment; and one from the last milk to pass through the equipment. The average amount of reduced ascorbic acid in the samples taken as described above was 18.6 mg., 17.1 mg., 5.9 mg., and 15.6 mg. per liter, respectively. It is evident from these data that different bottles taken from the same lot of freshly pasteurized milk may contain significantly different amounts of reduced ascorbic acid.

Acknowledgment

The author wishes to express his appreciation to Elliott Greenwood for collecting the milk samples and to Denzel J. Hankinson for his helpful comments and suggestions.

LITERATURE CITED

1. Brown, W. C., and Thurston, L. M. A review of oxidation in milk and milk products as related to flavor. *J. Dairy Sci.*, **23**, 629 (1940).
2. Elvehjem, C. A. Pasteurized milk. *Milk Plant Monthly*, **7**, 26 (1941).
3. Greenbank, G. R. The oxidized flavor in milk and dairy products: A review. *J. Dairy Sci.*, **31**, 913 (1948).
4. Holmes, Arthur D., Tripp, F., Woelffer, E. A., and Satterfield, G. H. A study of breed and seasonal variations in the ascorbic acid content of certified milk from Guernseys and Holsteins. *J. Nutrition*, **17**, 187 (1939).
5. Holmes, Arthur D., Jones, C. P., Wertz, A. W., Esselen, K., and McKey, B. V. The ratio of ascorbic, nicotinic, and pantothenic acids, riboflavin, and thiamin in late summer milk. *J. Dairy Sci.*, **27**, 849 (1944).
6. Holmes, Arthur D. Rate of destruction of reduced ascorbic acid in riboflavin-fortified pasteurized milk. *Food Technol.*, **4**, 92 (1950).
7. Kothavalla, Z. R., and Gill, H. S. The effect of various factors on the vitamin C content of the milk of cows and buffaloes. *Indian J. Vet. Sci.*, **13**, 35 (1943); *C. A.*, **39**, 2346 (1945).
8. Mawson, E. H., and Kon, S. K. Vitamin C content of milk as consumed. *Lancet*, **2**, 14-15 (1945).
9. Pratt, S. D. Does nickel dissolved from the container during pasteurization catalyze the destruction of the vitamins of milk? *J. Nutrition*, **3**, 141 (1930).
10. Reedman, E. J. The ascorbic acid content of milk. *Can. Pub. Health J.*, **28**, 339 (1937).
11. Reif, G., and Schormuller, J. Effect of rustproof steels on the vitamin C content of milk. *Pharmazie*, **2**, 545 (1947); *C. A.*, **42**, 2687 (1948).
12. Sharp, P. F. Rapid method for the quantitative determination of reduced ascorbic acid in milk. *J. Dairy Sci.*, **21**, 85 (1938).
13. Sharp, P. F., Trout, G. M., and Guthrie, E. S. Vitamin C, copper and the oxidized flavor of milk. *Milk Plant Monthly*, **26** No. 5, 32 (1937).
14. Sharp, P. F., and Hand, D. B. Riboflavin, vitamin C, and flavor of dairy products. *Proc. First Food Conference Inst. Food Tech.* (Garrard Press) **1**, 139 (1940).
15. Sherman, H. C., and Lanford, C. S. *Essentials of Nutrition.* 2nd Edtion 1943, MacMillan Company, New York, N. Y.
16. Stull, J. W., Herreid, E. O., and Tracy, P. H. A study of the use of the antioxidant nordihydroguaiaretic acid in dairy products, and its antioxygenic properties in milk. *J. Dairy Sci.*, **31**, 449 (1948).
17. Woessner, W. W., Weckel, K. G., and Schuette, H. A. The effect of commercial practices on ascorbic acid and dehydroascorbic acid (vitamin C) in milk. *J. Dairy Sci.*, **23**, 1131 (1940).
18. Woessner, W. W., Elvehjem, C. A., and Schuette, H. The determination of ascorbic acid in evaporated milk, powdered milk and powdered milk products. *J. Nutrition*, **20**, 327 (1940).

Designing Sanitation Into Food Plants[a]

A. T. WAIDELICH
Research Division, The Austin Company, Cleveland, Ohio

(Manuscript received March 12, 1951)

Sanitation problems in food industries are extremely varied and complex. There is little similarity, for instance, in the requirements of confectionary plants, packing houses, canneries, cereal mills, dairy industries and coffee roasting establishments.

Their one common problem is the necessity of maintaining immaculate cleanliness for the protection of their products on the most economical basis available. The public's faith in the purity of goods produced by our 36 billion dollar food processing industries certainly testifies to the thoroughness with which they have done their job, regardless of expense. Nevertheless, anything and everything which can be done to reduce the long term costs of ownership and operation are bound to be reflected in the unit cost of manufacture, the final selling price, and the profit account.

Facilities, equipment and space required to meet the problems of sanitation must be provided on an efficient and economical basis, with equal consideration for wearing qualities and the cost of maintenance as well as the initial cost of construction. All of the engineers concerned with the project will have to work and plan together to insure flexibility for the rearrangement of production lines and equipment, if necessary, without crowding that complicates the sanitarian's job.

New construction techniques, improved mechanical equipment and building materials now make it practical to tackle many sanitation problems at their source. These advances have paved the way for reduction of non-productive man-hours required to maintain sanitary standards.

While it is obviously to any firm's, as well as the public's, advantage to meet the needs for sanitation as economically as possible, one has to recognize that low first cost does not always result in the lowest final cost. Our problem, then, is to determine what factors contribute toward the attainment of highest quality at lowest cost.

The site may have a direct bearing on several aspects of the problem. A given site having ready access to raw materials, markets, and with favorable freight rates, power and fuel costs, and labor supply might, for instance, prove entirely impractical without the proper water supply and waste disposal. If much water is required for product cleaning, heat processing, cooling, fluming, washing containers, cleanup of plant and equipment, management will do well to give water supply serious consideration before final selection of a site. Incidentally, depletion of our water resources is becoming an ever-increasing headache.

Water from a municipal water supply system is frequently aceptable without secondary treatment. Water treatment costs so much in some localities that it should be avoided, unless other factors completely outweigh this factor.

The large volume and high biochemical oxygen demand of waste produced in many food processes makes disposal a particularly serious problem. Even after screening and pre-treatment it is frequently beyond the capacity of existing municipal sewage treatment plants. But most of these problems can be resolved if they are shared with persons expert in these fields at the outset. At the same time, problems of dust, smoke, rodents or insects in the vicinity must be considered along with the cost of safeguarding the plant against them.

DESIGNING THE PLANT

When it comes to food plant design, sanitation enters into every aspect of the planning. The location of plant services or service areas, with respect to processing departments, requires special care.

Dust, smoke and odors, for instance, cause contamination, which can be eliminated without any inconvenience or added cost by careful planning of boiler house, waste disposal plant, railroad sidings, truck docks, parking lots and roads.

Centralized operations under one roof frequently aid sanitation in several unobserved ways and usually offer a decided economical advantage over split layouts.

One building requires but half the wall area required by four of equal aggregate area. Unless separation of process is required, the one building with only half as much wall area will be easier to maintain. Even where areas must be separated by partitions, one structure generally reduces both materials handling distances and exposure to outside contaminants. Thus for the same capital investment, better sanitary facilities can usually be provided if the whole manufacturing area is enclosed within one building, which will be more economical to heat and air-condition.

The actual choice of a cross-section between single-story and multi-story buildings, column spacing and character of the spans, all have their bearing on the plant's ability to cope with various aspects of sanitation.

Many of the advantages which have led to the adoption of single-story layouts in other industries apply equally to a large percentage of the food processing industries, which traditionally have been housed in multi-story buildings. While some special process requirements like cereal milling can probably be met to better advantage by the use of gravity flow than in any horizontal floor arrangement, multi-story structures present many special sanitary problems. Stairs and elevator shafts required in such buildings are hard to clean.

Single-story structures, for instance, require much less exposed piping, particularly for floor drainage, so that there is less likelihood of contaminating the product by condensation drip or leaks from faulty joints. There are fewer pipe sleeves in which vermin may hide and breed, and floor drainage systems

[a] Presented at the Tenth Annual Meeting of the IFT, Chicago, Illinois, May 24, 1950.

employing wide, shallow, easy-to-clean, drainage trenches with removable gratings are practical.

Water vapor, steam, and odors produced in single-story structures may be removed directly through roof ventilators immediately above process equipment without duct-work which is difficult to keep clean.

Handling of bulk containers and disposal of refuse are easier when everything is at ground level. Sometimes fluming is an economical and sanitary method of waste removal.

The wider spans provided in single-story plants mean fewer columns and incidentally less opportunity for bacterial growth around the column bases. Process equipment can be more easily accommodated, piping can be concentrated in sub-floor areaways, so that there is an absolute minimum of obstruction in the production areas, and air-conditioning ducts can sometimes be located against the roof.

Spans of 50, 60, 70 and 80 feet with columns 40 to 60 feet apart in the other direction are now commonplace. They provide unobstructed floor areas with maximum flexibility for layout changes and elbow room for cleaning.

The horizontal flow of a single-story process may result in a more efficient layout than could be obtained by the use of gravity flow in a multi-story structure. It warrants careful consideration and often permits simpler and more efficient materials handling, resulting in less movement and faster flow, both highly desirable where a food product is subject to adulteration. The mere movement of the product from raw storage through the various stages of production to storage of the finished product adds nothing to its value. Excessive handling may even detract from that value, as contamination and damage due to handling promote spoilage. Faster handling methods make possible equal production with fewer people and the possibility of contamination by human contact is thereby reduced. The likelihood of contamination due to airborne sources is also less.

Once a decision has been reached on the cross-section to be used, it is important to keep sanitation in mind at every step in development of the detailed layout. In nine cases out of ten, a compact straight-line arrangement of the production facilities will not only result in more production with less equipment and less labor, but will reduce the cost of maintenance and promote a high level of sanitation at minimum cleaning cost.

In the food industries, the choice of materials used for finishing the interior bears a more important relationship to product quality and production cost than in any other field, with the possible exception of pharmaceutical manufacture.

Before choices are made, each surface in a plant should be analyzed to determine the functions it is expected to perform. Floor, wall, and ceiling surfaces in food processing areas must not only be able to resist various organic fats, acids, and alkalies produced by the food products, but must also be resistant to strong cleaning solutions and abrasion.

Where no moisture is employed or produced by the process, and dry cleaning methods are used for cleanup, as in bakeries, hard wood strip or block flooring may be perfectly satisfactory for floors. In the dairy industry, on the other hand, where fats, lactic acids and the like are present, floors must be constructed of acid-proof brick or tile, the weak point of this type floor being the joints.

Specially formulated cementing materials, designed to resist sugar, acids, alkalies, oils, etc., are now commercially available and, if carefully selected and applied in narrow tile and brick joints, will successfully resist any condition which may be encountered in food plants.

Extreme care is required in the detailing of floors to prevent the failure of joints or the opening up of cracks which hasten disintegration and afford a seat for bacterial growth.

Special care in the preparation of sub-grades, and the addition of sufficient reinforcing steel to resist the tensile stresses induced by temperature change or shrinkage, will prevent the cracking of concrete floors which can be rendered impervious by the use of surface hardeners which resist abrasion and dusting.

Glazed structural facing tile has won widespread acceptance as the ideal sanitary wall surfacing material. It resists moisture, chemicals, and just plain dirt, and is available in colors which make it possible to maintain attractive, sanitary surroundings at minimum cost.

Other materials — such as unglazed tile, or glass, glass block, brick, metal, plaster, concrete, and asbestos cement board —may, however, be used very successfully under certain conditions, the latter five usually with a suitable paint. Whatever the material used, walls should, insofar as possible, be light in color and free of moldings, window ledges and other projections, which catch dirt and are easily overlooked in day-to-day cleaning.

Coved bases at wall and floor intersections will prevent the accumulation of dirt, grease and slime which is hard to remove. The use of light colors automatically calls attention to dirt of all kinds and is the quickest way to insure its removal.

Plant lighting must insure the constant exposure of dirt, rodents, or anything else which might result in contamination of the product. The shifting character of daylight leaves no alternative to primary dependence on artificial sources for this lighting. Since it is hard to find dirt in the shadows, and factory sweepers, unlike some of these new-fangled vacuum cleaners, don't wear footlights on their shoes, it is up to the lighting engineers to provide well-diffused general lighting of sufficient intensity to insure cleanliness. This usually means fluorescent lighting, with intensities ranging all the way from 35 to 100 foot-candles.

The removal of dust and dirt, bacteria and odors are the primary concern in maintenance of atmospheric sanitation.

If circumstances require filtering of all incoming air, electrostatic precipitators will probably give best results. High efficiencies ranging from 85 to 90% are claimed for this type filter. Use of impingement type filters placed in the air stream ahead of the electrostatic filter is recommended to increase its efficiency by removing the larger dust particles and to provide some filtering in event of power failure.

If odor creates a problem, the most practical means of control is by exhausting the foul air near the source and introducing fresh air to replace it. If this procedure calls for the removal of air in large quantities during cold weather, when this procedure would greatly increase the cost of heating, the same ends can be accomplished by re-circulating the air through activated carbon cannisters, which absorb the odors in the same way as a sponge soaks up water. These become saturated after absorbing approximately 20% of their own weight, but may be reactivated at a reasonable cost.

Where humidity control or summer air-conditioning are not required, winter heating requirements can be most effectively met, from the standpoint of sanitation, by the use of blower-type unit heaters or by radiant panel heating with hot water pipes imbedded in the

floors. There are no hiding places for dirt or rodents in such systems.

An increasing number of food plants, however, are either installing or preparing themselves for future installation of full year-round air-conditioning. The duct work in such systems calls for special precautions, such as the installation of mechanical filters at inlets and outlets and germicidal lamps in the ducts for protection against air-borne bacteria.

The costs of providing for such atmospheric control, with or without air-conditioning, can frequently be held to a minimum by the use of standard factory-built equipment, which can be installed on platforms that form an integral portion of the building structure. If all of the equipment can be assembled right on such platforms at floor level and raised into position up in the building trusses as a single unit, instead of piece by piece, a considerable saving will result.

One may include initially as much or as little as desired in way of atmospheric control equipment on such platforms, which are frequently designed with a minimum of equipment for merely filtering and moving the air, but with provision for future addition of refrigeration and other supplementary units. In each instance, the extent of the installation is usually controlled by considering the economy of the operation and balancing it against the advantages to be gained through improved sanitation or better working conditions.

Important as the physical aspects of sanitation are, one cannot afford to overlook the aesthetic and psychological factors when designing a food plant. Good architectural design and clean-cut appearance exact a marked influence on the attitudes and habits of plant personnel, on whom the maintenance of standards depends.

In the final analysis, the attainment of desirable standards of sanitation in any food plant, and the cost of maintaining them, will depend upon the thoroughness with which all of the problems of design, engineering and continuing maintenance have been analyzed in advance. It stands to reason that no plant will be any better than the combined background, ability and experience of all the men entrusted with the responsibility for planning it.

Comparative Evaluation of Spices. III. Flavor Retention of Natural Spices and of Spice Oils and Spice Extractives After Boiling and Baking[a]

ROBERT A. NANZ[b] AND L. C. CARTWRIGHT
Foster D. Snell, Inc., New York, N. Y.

(Manuscript received April 21, 1950)

The ability of natural spices and of spice oils, oleoresins, and extractives sorbed on salt and sugar to retain their qualities through processing was studied by means of the organoleptic panel evaluation of flavor, color, and texture. The flavoring materials were added to white sauce, oil white sauce, and certain representative foods as pumpkin and cream sauce, and these foods boiled before evaluation. Comparisons were also made in chopped ham, chopped pork, and certain selected types of bread, muffins, and yeast raised rolls. Methods of scoring and statistically-analyzed scores are given.

Panel evaluation of these heat-treated materials shows that in foods so cooked, more volatilization loss or flavor destruction occurs in the use of spice oils and extractives than with natural spices. Both natural spices and spice oils, extractives, etc. are extensively used in the food industries. Both types of seasoning materials have their merits, as is common knowledge to food technologists.

How well natural spices retain their flavor through food processing, in comparison with the flavor retention of spice oils and extractives, is necessary information for the food manufacturer. An extensive and comprehensive survey of the literature on spices has failed to disclose any such direct comparison under controlled processing conditions *(3)*.

Therefore, the evaluation of quality changes that may occur in the flavors imparted to foods by both natural spices and spice oils and extractives during heating as in boiling and baking were studied. In the present study, the following types of materials were compared: (a) natural ground spices; (b) spice oils and oleoresins; (c) spice oils and oleoresins with added emulsifying agents; and (d) extractives from spices blended with sugar or salt as a base.

EXPERIMENTAL PROCEDURE

Methods of Evaluation. As cited in our previous studies *(1, 2)*, the evaluation of spice-flavored foods requires a familiarity with the flavor of each spice alone, tasted directly. In developing this ability, the panel evaluated spices, spice oils and extractives in certain test foods *(1)* whose formulas had been carefully devised.

Accepted panel evaluation technics were used. Statistical checking of the validity of the scoring confirmed the reliability of the method, indicating that the blindfold method was unnecessary. This previous rechecking included masked standards, the use of higher levels of flavorings than the manufacturer's recommendations, and statistical analysis of scores. The original evaluation method stood the test well and its reliability was established *(3)*.

Test Foods. Boiling of the test foods containing the flavoring materials was carried out in open beakers, by controlled heating in a boiling-water bath with stirring to ensure uniform heating. The water lost by evaporation was replaced. These

[a] This work was sponsored by the American Spice Trade Association as part of their program to obtain fundamental spice information.

[b] Present address: Florida Citrus Canners Cooperative, Lake Wales, Florida.

boiling tests are a re-evaluation of the results obtained in previous studies *(2)* in which similar spice levels were used. Eggnog, used for the evaluation of mace and nutmeg in the previous studies was replaced by pumpkin mix for the present boiling studies. Upon cooling, the mixtures were evaluated by the panel.

Baking of cereal products as bread, muffins, pie crust and rolls was carried out as a second phase of this stability study. Selected spices were evaluated in the following foods: caraway in rye bread; cassia in yeast-raised rolls; cloves in muffins; coriander in pie crust; ginger in gingerbread (also called gingercake); mace in yeast-raised sweet rolls; and nutmeg in yeast-raised sweet rolls. Rye bread was prepared by a standard cook book recipe. Ground caraway and the extractives on salt and sugar bases were mixed directly into the dough along with the dry ingredients used in the first portion, the sponge. The liquid spice extracts were added with the liquid ingredients. After mixing and raising, the unit loaves were baked at 191° C. (375° F.) for one hour. Evaluation followed cooling.

Yeast-raised rolls were made with a prepared, packaged ready-mix. Following the directions on the package, the dry spice materials were added along with the dry components and the liquid spice extractives or mixtures added with the liquid ingredients, and the rolls were baked at 204° C. (400° F.) for 15 minutes. Evaluation followed when cooled. Cassia materials were blended into the rolls as stated. Mace and nutmeg materials were incorporated, along with added sugar, making sweet rolls as directed on the package.

Muffins were made with a hot muffin ready-mix (baking powder raised type). Clove materials were added as in the yeast rolls. The muffins were baked at 191° C. (375° F.) for 25 to 30 minutes.

Pie crust was made from a ready-mix, the coriander materials being added as in the other baking mixtures. The pie crust was rolled out to normal thickness, divided into units each containing a separate spice material, and baked flat at 232° C. (450° F.) until brown, or approximately 15 minutes.

Gingerbread was made by a standard cook book recipe, using dark molasses and baking soda as components of the dough mixture. Ginger materials were added in the same manner as in previous baking mixtures. The batter was baked at 177° C. (350° F.) for 45 minutes.

In order to determine the proper levels to give the best comparison of the different seasoning materials used, trial bakes were made for each spice, using the natural spice materials at four levels. The most acceptable level for each spice was selected, based on the opinion of four judges. After having established these levels, the above-mentioned test bakes were made for panel evaluation, using the spice extractives in proper proportion to the natural spices, based on the manufacturers' recommended table of equivalents. The levels selected are shown in Table 1.

TABLE 1

Levels of Seasoning Materials Used in Baked Cereal Products

Spice	Natural spice	Extractives on salt and sugar bases	Oils	Oils with added emulsifying agents
	% by weight	*% by weight*	*% by weight*	*% by weight*
Caraway	3.0	1.5	0.15	0.15
Cassia	1.1	0.6	0.011	0.022
Clove	0.6	0.6	0.102	0.12
Coriander	4.0	2.0	0.02	0.04
Ginger	0.8	0.4	0.04	0.04
Mace	0.7	0.5	0.088	0.042
Nutmeg	0.7	0.5	0.088	0.042

Chopped ham and ground fresh pork were the baked meat products used. Chopped ham was prepared by using commercially canned hams, carefully separated into lean and fat. Ninety percent lean and 10% fat were blended after being finely ground. Salt and sugar, in specified amounts, were blended into the entire batch with the exception of the portions containing the extractions sorbed on sugar or salt. Compensations were made for these additions, making the levels of sugar and salt the same for all portions. The formula used for the chopped ham mixture was: finely ground canned ham (90% lean, 10% fat), 99.7 weight parts; sugar (except in unit testing extractive on sugar base), 0.3 weight parts; spices and spice extractives, in specified amounts added to 100 g. portions of the sugar and ham mixture.

A portion of the fat from a unit volume of the chopped ham mixture was held out and used as a small "cup" into which was weighed the liquid spice extractive. By this means, and with careful mixing, the additions were evenly distributed in the ground ham.

In determining the proper level of natural ground spice to be added to chopped ham, and in the subsequent tests with ground pork, the panel was offered samples of the meat prepared and cooked with three or four levels of the spice. For example, black pepper in pork was tried in the following percentages by weight: 0.8, 1.0 and 1.2. It was found that 0.8% was too weak for most effective evaluation of its full flavor quality and 1.2% was too strong for best evaluation. Therefore, 1.0% was used in the comparative tests.

With cassia added to chopped ham, levels of 1.6, 2.0 and 2.4% by weight were tried. In like manner, 2.0% was considered "just right" by the panel. This preliminary testing was carried on with natural spices only. The manufacturers' recommendations of strengths equivalent to the selected levels of natural spices was used as a basis for determining the levels of the spice oils and extractives as given in the table. Preliminary testing showed that the levels shown in Table 2, of these seasoning materials in chopped ham gave satisfactory comparisons.

TABLE 2

Levels of Seasoning Materials Used in Chopped Ham

Spice	Natural spice	Extractives on salt and sugar bases	Oils	Oils with added emulsifying agents
	% by weight	*% by weight*	*% by weight*	*% by weight*
Cassia	2.0	1.07	0.02	0.04
Cloves	0.5	0.5	0.085	0.10
Ginger	1.2	0.6	0.06	0.06
Mace	1.0	0.75	0.125	0.06
Nutmeg	1.0	0.75	0.125	0.06

The ham mixtures were formed into cakes and baked in sections of muffin tins for 15 minutes at 177° C. (350° F.) in an electric oven, and evaluated when cool enough to taste.

Chopped pork was prepared in the same manner from fresh loin of pork, using 80% lean and 20% fat. The mixtures were baked for 20 minutes at 177° C. (350° F.) and evaluated when cool enough for tasting.

The formula used for the pork mixture was: finely ground fresh pork (80% lean, 20% fat), 97.7 to 99.7 parts by weight; salt (except in unit testing extractive on salt base), 1.0 part by weight; sugar (except in unit testing extract on sugar base), 0.3 part by weight; black pepper (except in black and white pepper testing), 1.0 part by weight; spices, and spice oils and extractives, in specified amounts, added to 100 g. portions of mixture.

Spice oils and extractives were used in levels based on equivalents given by the manufacturers, as in previous tests. The levels of seasoning materials, found satisfactory for proper evaluation in pork are shown in Table 3.

TABLE 3

Levels of Seasoning Materials Used in Pork

Spice	Natural spice	Extractives on salt and sugar bases	Oils	Oleoresins	Oils with added emulsifying agents	Oleoresins with added emulsifying agents
	% by weight	*% by weight*	*% by weight*	*% by weight*	*% by weight*	*% by weight*
Capsicums, hot	0.3	0.15	.....	0.024	.....	0.024
Capsicums, mild	1.0	.....	.....	0.08	.....	.....
Caraway	3.0	1.5	0.15	.....	0.15	.....
Coriander	5.0	2.5	0.025	.....	0.05	.....
Mustard	2.0	.....	0.016	.....	0.01	.....
Paprika	4.0	.....	.....	0.32	.....	.....
Pepper, black	1.0	0.74	0.016	0.06	0.020	0.020
Pepper, white	1.2	0.89	.....	.....	0.024	.....
Sage	1.2	0.4	0.024	.....	0.048	.....

An adjusted scoring form was used in the evaluation of these meat mixtures. In all cases the evaluation was carried out by a "blindfold" technic, with no identified natural spice mixture used as a standard. As a control the meat mixture containing no seasoning material was included, principally to detect texture difference produced by the added seasoning materials. The scores used were as follows:

Factor	Value	Criterion
Odor strength	20	Of spice in the meat
Odor quality	20	Desirability of spice odor, absence of off-odors
Taste strength	20	Of spice in the meat
Taste quality	20	Desirability of spice tastes, absence of off-tastes
Color strength	10	Appealing, no unusual color intensity
Color quality	10	Appetizing, pleasant, normal color

In addition, all products were scored for uniformity of preparation. Fifty points each were given for "mastication" (softness, juiciness, and ease of chewing), and for "texture" (fibrous, stringy, greasy, and granular characteristics).

RESULTS

Table 4 shows the mean score and the standard error of the mean (SEM) for each seasoning material. Low standard errors predominate. Under the experimental condition used, the natural spices appear to have a superior flavor stability as tested after boiling in an aqueous medium.

Table 5 shows the mean scores and standard errors of the mean for the results of the evaluation after boiling in an oily medium. These results show that spice oils and extractives, used in the proportions indicated, do not have the flavor stability of natural spices in this type of test.

TABLE 4

Evaluation of the Flavor Stability of Spices and Spice Extractives and Oils in White Sauce After Boiling for One-half Hour

Spice	Flavor scores									
	Natural spice [e]	Extractives on salt and sugar bases		Oils		Oleoresins		Oils with added emulsifying agents		Oleoresins with added emulsifying agents	
		SEM, ±		SEM, ±		SEM, ±		SEM, ±		SEM, ±	
Capsicums, hot, dom.	90	81	1.4	....	....	84	2.5	....	....	81	2.6
Capsicums, mild, dom.	90	....	....	....	....	88	1.3	....	....	....	....
Caraway	90	58	3.8	80	3.6	....	....	72	3.2	....	....
Cassia	90	67	2.9	62	1.4	....	....	57	1.0	....	....
Cloves	90	71	2.4	74	2.9	....	....	66	3.1	....	....
Coriander	90	82	3.5	82	2.3	....	....	81	4.4	....	....
Ginger	90	53	2.8	76	1.7	....	....	72	1.3	61	2.7
Mace	90	69	3.6	84	2.2	....	....	72	3.7	....	....
Mustard	90	....	....	88	1.3	....	....	86	3.0	....	....
Nutmeg	90	77	3.1	80	4.8	....	....	80	2.8	....	....
Paprika, dom.	90	....	....	80	3.7	....	....	....	....	....	....
Pepper, white	90	83	0.7	....	....	....	....	83	3.5	....	....
Pepper, black	90	81	4.9	86	3.9	84	3.4	81	4.5	82	3.4
Sage	90	75	4.2	70	4.5	....	....	62	3.6	....	....

[e] The natural spices were all given a standard score of 90 on the basis of 100 as a maximum. This makes possible a higher figure for comparative values for other samples, if the samples should have a higher spice quality than that of the natural spices.

TABLE 5

Evaluation of the Flavor Stability of Spices and Spice Extractives and Oils in Oil White Sauce After Boiling for One-half Hour

Spice	Flavor scores									
	Natural spice [d]	Extractives on salt and sugar bases		Oils		Oleoresins		Oils with added emulsifying agents		Oleoresins with added emulsifying agents	
		SEM, ±		SEM, ±		SEM, ±		SEM, ±		SEM, ±	
Capsicums, hot, dom.	90	82	3.3	....	....	79	2.6	....	....	80	2.7
Capsicums, mild, dom.	90	....	....	....	....	85	3.1	....	....	....	....
Caraway	90	75	4.9	83	2.5	....	....	83	1.9	....	....
Cassia	90	60	1.9	68	2.7	....	....	58	1.6	....	....
Cloves	90	68	2.5	81	3.8	....	....	68	3.3	....	....
Coriander	90	81	1.0	76	1.5	....	....	74	4.0	....	....
Ginger	90	62	1.9	67	3.4	....	....	64	3.9	62	2.8
Mace	90	76	2.9	88	0.9	....	....	79	1.7	....	....
Mustard	90	....	....	73	3.3	....	....	74	1.7	....	....
Nutmeg	90	71	3.4	85	3.0	....	....	70	4.1	....	....
Paprika, dom.	90	....	....	....	....	81	3.4	....	....	....	....
Pepper, white	90	77	2.1	....	....	....	....	79	3.5	....	....
Pepper, black	90	76	3.1	76	5.1	75	3.7	74	3.8	72	4.2
Sage	90	68	3.0	86	2.9	....	....	76	1.9	....	....

[d] See footnote for Table 4.

Table 6 shows the results of evaluations in the selected test foods. Under the conditions used, the natural spices again appeared to be superior in boiled foods.

Evaluation in baked cereal products gave similar results as indicated in Table 7. In this test the spice oils and extractives scored considerably lower than the natural spices in most cases.

The scoring of seasoning materials in chopped ham is given in Table 8. None of the spice oils and extractives had quality ratings as high as the natural spices when used in the concentrations indicated. Mastication

TABLE 6

Evaluation of the Stability of Various Seasoning Materials in Cream Sauce or Pumpkin After Boiling for One-Half Hour

Spice	Test food	Flavor scores									
		Natural spice [e]	Extractives on salt and sugar bases		Oils		Oleoresins		Oils with added emulsifying agents		Oleoresins with added emulsifying agents	
			SEM, ±		SEM, ±		SEM, ±		SEM, ±		SEM, ±	
Capsicums, hot, dom.	Cream sauce	90	68	1.9	....	....	....	....	70	0.6	63	1.8
Capsicums, mild, dom.	Cream sauce	90	....	....	....	....	....	....	89	0.8	....	....
Caraway	Cream sauce	90	64	1.3	86	1.4	....	....	78	2.2	....	....
Cassia	Pumpkin	90	78	2.4	77	2.7	....	....	68	3.3	....	....
Cloves	Pumpkin	90	63	1.9	76	1.0	....	....	62	1.4	....	....
Coriander	Cream sauce	90	77	1.6	76	1.7	....	....	71	1.5	....	....
Ginger	Pumpkin	90	68	1.5	72	2.5	....	....	71	1.7	65	0.8
Mace	Pumpkin [f]	90	84	3.0	85	2.6	....	....	85	1.6	....	....
Mustard	Cream sauce	90	....	....	78	3.0	....	....	70	3.1	....	....
Nutmeg	Pumpkin [f]	90	75	2.2	87	1.6	....	....	84	3.0	....	....
Paprika, dom.	Cream sauce	90	....	....	....	....	79	3.6	....	....	....	....
Pepper, white	Cream sauce	90	77	3.4	....	....	....	....	77	1.2	....	....
Pepper, black	Cream sauce	90	72	2.6	85	2.7	86	1.8	88	2.1	76	1.0
Sage	Cream sauce	90	58	2.0	70	2.4	....	....	75	2.2	....	....

[e] See footnote to Table 4.
[f] Used in preference to eggnog for boiling test.

TABLE 7

Evaluation of the Flavor Stability of Seasoning Materials in Cereal Food Products After Baking

Test system	Flavor scores											
	Natural spice		Extractives on salt and sugar bases		Oils		Oleoresins		Oils with added emulsifying agents		Oleoresins with added emulsifying agents	
	SEM, ±		*SEM*, ±		*SEM*, ±		*SEM*, ±		*SEM*, ±		*SEM*, ±	
Caraway in rye bread, 191° C. (375° F.), 60 min.	90	2.5	66	1.3	78	1.8	....	....	74	2.3	....	....
Cassia, in yeast-raised rolls, 204° C. (400° F.), 15 min.	90	0	63	5.7	56	1.9	....	....	61	5.0	....	....
Cloves in muffins, 191° C. (375° F.), 30 min.	90	0	63	3.0	73	2.6	....	....	62	1.5	....	....
Coriander in pie crust pastry, 232° C. (450° F.), 15 min.	90	0	82	1.2	79	2.5	....	....	82	3.3	....	....
Ginger in gingerbread, 177° C. (350° F.), 45 min.	90	0	65	2.9	79	2.9	....	....	74	4.7	71	5.3
Mace in sweet rolls, 204° C. (400° F.), 15 min.	90	0	75	2.6	80	1.8	....	....	74	1.9	....	....
Nutmeg in sweet rolls, 204° C. (400° F.), 15 min.	90	0	64	5.3	74	0.1	....	....	64	4.2	....	....

TABLE 8

Evaluation of the Flavor Stability of Seasoning Materials in Chopped Ham After Baking for 15 Minutes at 177° C. (350° F.)

Spice	Flavor scores											
	Natural spice		Extractives on salt and sugar bases		Oils		Oleoresins		Oils with added emulsifying agents		Oleoresins with added emulsifying agents	
	SEM, ±		*SEM*, ±		*SEM*, ±		*SEM*, ±		*SEM*, ±		*SEM*, ±	
Cassia	88	1.3	76	3.3	68	1.1	....	....	58	2.8	....	....
Cloves	90	1.3	68	2.8	82	2.6	....	....	75	5.2	....	....
Ginger	88	2.8	79	4.1	86	1.3	....	....	82	2.6	79	4.1
Mace	89	1.0	73	2.7	86	0.8	....	....	66	1.8	....	....
Nutmeg	90	1.6	61	3.6	86	1.5	....	....	72	2.4	....	....
	Mastication and texture											
Cassia	90	0	88	2.5	88	2.5	....	....	89	1.5	....	....
Cloves	90	0	90	0	90	0	....	....	90	0	....	....
Ginger	90	0	90	0	90	0	....	....	90	0	....	....
Mace	90	0	90	0	90	0	....	....	90	0	....	....
Nutmeg	90	0	90	0	90	0	....	....	90	0	....	....

and texture was altered only slightly by the use of cassia oil and extractives. All the other seasoning materials had no variation in this respect.

Chopped pork was used to evaluate the remainder of the seasoning materials. The results of this scoring are given in Table 9. Natural spices scored highest in all cases, except for an equal rating shown by capsicum on a salt base. Mastication and texture were uniform in all cases, and therefore the resulting ratings of 90 for all materials were not included as part of Table 9.

The standard error of the mean given throughout these tables serves to show the degree of agreement of the panel members in arriving at the mean score given.

TABLE 9

Evaluation of the Flavor Stability of Seasoning Materials in Chopped Pork After Baking for 20 Minutes at 177° C. (350° F.)

Spice	Flavor scores											
	Natural spice		Extractives on salt and sugar bases		Oils		Oleoresins		Oils with added emulsifying agents		Oleoresins with added emulsifying agents	
	SEM, ±		*SEM*, ±		*SEM*, ±		*SEM*, ±		*SEM*, ±		*SEM*, ±	
Capsicums, hot, dom.	88	2.0	88	1.8	....	....	93	4.2	....	....	86	2.3
Capsicums, mild, dom.	90	0.4	....	....	....	....	87	1.3	....	....	....	....
Caraway	88	1.9	76	3.3	86	1.4	....	....	82	3.3	....	....
Coriander	88	2.5	71	4.9	83	3.9	....	....	77	3.9	....	....
Mustard	90	0	....	....	79	1.1	....	....	82	1.1	....	....
Paprika, dom.	89	0.9	....	....	....	....	78	5.2	....	....	....	....
Pepper, black	90	0	79	4.3	80	2.9	82	0.5	78	4.6	75	5.2
Pepper, white	85	5.4	80	7.2	....	....	....	....	82	4.4	....	....
Sage	90	1.0	73	6.0	87	4.1	....	....	85	4.2	....	....

In general, these standard errors of the mean are significantly low.

Evaluation of spices and spice oils and extractives in test foods can be done accurately and reproducibly by panel methods. Scores from a four-member panel evaluation, analyzed statistically, give a reliable picture of the comparative quality of the flavor of these spices and spice oils and extractives as evaluated in selected test foods after boiling or baking. It can be said that ultimate consumer acceptance of spice-flavored processed foods is reflected by the results of these critical evaluations.

Seasoning materials of the type prepared from natural spices by extraction or other processing as with oils or oleoresins, with or without added emulsifying agents, and of one type added to a salt or sugar base, are in general of inferior odor and flavor quality when added to representative foods and heat-processed by boiling or baking. The foods studied in the present work encompass the plain water type, oil-in-water emulsion type, or types combining more complex components and normal fiber bases—pumpkin, cream sauce, ham, pork, and cereal products.

It is evident that, at the temperatures of some 100° C. (212° F.) reached in this processing, natural spices are able to retain more of their odor and flavor qualities and will undergo less loss due to volatilization and less odor and flavor destruction than do the extractives. This is related to the lack of normal cellular structure and normal constituents in the extractives.

In no case was the presence of ground natural spice particles considered an undesirable adjunct to the food. In fact, their absence made many of the foods look unnatural. For instance, muffins without cloves were colorless, pork without the appearance of natural pepper looked drab, and rye bread without caraway was pale.

SUMMARY

Spices and spice oils and extractives were comparatively evaluated in white sauce, oil white sauce, and in representative foods (a pumpkin mixture and a cream sauce) after boiling and in meat products, such as chopped ham and chopped pork; and in cereal products, such as yeast-raised rolls, bread, and muffins after baking.

Panel evaluation of the cooked materials shows that, when used in the described proportions and under the specified experimental conditions, the odor and flavor quality and stability of natural ground spices were superior. Cooking foods at elevated temperatures causes

the least loss through volatilization and flavor destruction in the foods prepared with the natural spices.

Acknowledgment

The cooperation and suggestions of the members of the Research Committee of the American Spice Trade Association have been helpful. The members of the flavor evaluation panel, in addition to the authors, were Patricia Hugh Kelley, G. Dan Bynum, and S. J. Sica. Some of the statistical analyses were made by S. J. Sica.

LITERATURE CITED

1. Cartwright, L. C., and Nanz, R. A. Flavors improved, sales boosted through organoleptic tests. *Food Inds.*, 20, 1608 (1948).
2. Cartwright, L. C., and Nanz, Robert A. Comparative evaluation of spices. *Food Technol.*, 2, 330 (1948).
3. Nanz, Robert A., Tyler, Cornelia A., and Cartwright, L. C. Comparative evaluation of spices. II. Flavor evaluation of natural spices and spice substitutes in representative test foods. *Food Technol.*, 4, 252 (1950).

A Comparison of Three Methods for Determination of Moisture in Sweet Corn

C. E. GEISE, P. G. HOMEYER and R. G. TISCHER[a]

Department of Horticulture, Iowa State College, Ames, Iowa

(Manuscript received March 2, 1951)

Comparative moisture tests have been made on five varieties of sweet corn over the range of 62-79%. The vacuum oven method used as a standard was compared with results obtained using the Brown-Duvel and the Steinlite instruments. Results indicate that the Steinlite instrument is well adapted for simple rapid determination of the moisture content of sweet corn for canning.

For each determination by the vacuum oven method, 3 are required for the Steinlite and 9 for the Brown-Duvel to obtain results of equivalence.

Moisture content of sweet corn has been established as a reliable index for maturity in the canning stage by Culpepper and Magoon *(3)*, Huelsen and Michaels *(4)*, Jenkins and Sayre *(5)*, Kramer, Guyer, and Ide *(6)*, Kramer and Smith *(7)* and Pratt *(8)*. Maturity appears to be a summation of chemical and physical factors which depend on the period, during the growth of the plant, in which they are determined. Determinations of indexes of maturity have taken a wide variety of forms. Among the earlier methods which gained prominence were the thumb nail test, puncture tests and measurements of density. The measurement of the starch-sugar ratio in corn has been used as an index of maturity but has not come into wide use because the methods of analysis require too much time and technical skill. Other methods have been proposed including (1) measurement of alcohol insoluble solids, (2) measurement of the refractive index of expressed corn juice, (3) vacuum drying, (4) oven drying without vacuum, (5) removal of moisture by oil or solvent distillation (Brown Duvel method) and (6) measurement of the volume of juice squeezed from a sample of corn under standardized conditions (succulometer).

A new method has recently been introduced by the Fred Stein Laboratories for measuring the moisture in corn samples electrically. The moisture from a weighed sample is dissolved in a known volume of hygroscopic solvent. The solvent containing the moisture from the corn sample is used as the dielectric constituent in a coaxial cylindrical condenser. Changes in the dielectric characteristics of the solvent-corn extract mixture correspond with changes in the moisture content in the corn sample. The resulting alteration in the radio frequency impedance of the condenser is measured by an electronic oscillator as a change in frequency in the circuit. This change in frequency may be read from a meter and, after calibration, interpreted in terms of the moisture content of the sample. Since this operation may be completed in a very short period of time, it is important to determine the accuracy which may be expected in the use of this instrument in a quality control laboratory. The Brown-Duvel moisture tester and the vacuum oven were chosen for a comparison with the Steinlite moisture tester. The Brown-Duvel method was chosen because it has been widely used in the canning industry and the vacuum oven because of its general dependability as a laboratory instrument.

EXPERIMENTAL PROCEDURE

In making the comparison, five varieties of corn were used. These were Golden Cross Bantam, Golden Glory, Tendermost, Victory Golden, and Iochief. Golden Cross and Tendermost were selected because they are varieties commonly grown in the midwestern states for canning while the others, Golden Glory, Victory Golden, and Iochief are promising new hybrids which have recently been introduced. Daily samples of these varieties were obtained from experimental plots grown on the Horticulture Farm at Ames. Samples were harvested in the morning and brought immediately to the laboratory for husking and cutting. The silks were removed using a laboratory size screen silker.

Although water is used at several points in the canning procedure, none was used in the preparation of these samples to avoid apparent changes in moisture content which might be expected if wash water remained on the kernels. The cut kernels were packed in No. 2 C-enamel cans, sealed under mechanical vacuum, and rapidly frozen in an immersion freezer at —45.6° C.

[a] Journal Paper No. J-1914 of the Iowa Agricultural Experiment Station, Ames, Iowa, Project No. 1052.

(—50° F.). The frozen samples were stored at —17.8° C. (0° F.) until tests were completed.

The frozen samples were retained until the completion of the canning operation when they were analyzed for moisture content by the three methods being compared. Samples for the vacuum oven of approximately 10 g. were weighed out on a torsion balance to ± 0.01 g. Vacuum oven determinations were made on samples which were pre-dryed in an air oven at 80° C. (176° F.) for a five hour predrying period to prevent excessive boiling under vacuum. The partially dried samples were then dried for five hours in the vacuum oven at 95° C. (203° F.) under a vacuum of 30 inches of mercury. At the completion of the drying period, samples were removed to a desiccator to cool, then weighed, and the moisture content of the sample calculated in percent.[b]

Brown-Duvel determinations were made using 20 gram samples. Weighing was done on a torsion balance to ± 0.1 g. The distilling flasks were pre-conditioned each day by running a blank determination with corn before operations were begun. The oil-corn mixture was heated to 190° C. (374° F.) when the source of heat was removed. The distillate was then collected in 25 ml. graduated cylinders calibrated to read to 0.01 ml. The results were expressed as percent moisture by multiplying the number of milliliters of distillate by a factor of five.

Samples prepared for the Steinlite instrument were of approximately 10 g., weighed to 0.01 g. accuracy on a torsion balance. Accuracy of 0.01 in the weighing of the sample was prescribed for this method by the manufacturer of the instrument; whereas, accuracy of 0.1 g. in weighing samples for the Brown-Duvel was sufficient in the commercial procedure being followed.

Tared squares of cellophane were used in conveying the weighed samples to the blendor. Cellophane was used since it is sufficiently impervious to moisture and is easily macerated in the blending operation. The use of pliofilm was attempted, but the elastic properties prevented its maceration and it wrapped around the blendor knives in such a manner as to decrease the efficiency of blending.

In accordance with the objective of this investigation, the operating instructions of the Steinlite moisture tester were adhered to with the exception of sample preparation. Moisture was released from the kernels upon thawing of the frozen samples; therefore the entire frozen sample was blended in order to obtain a homogeneous sample. Whole kernels, cut from the cob, constituted the recommended sample. The prepared sample and tared square of cellophane were transferred to a one-half pint mason jar to which 100 ml. of the solvent, Aquafin No. 1, was added. The mason jar and the knives of an Osterizer were assembled and the sample blended for two minutes. The moisture was filtered through Eaton and Dikeman No. 615 filter paper, an open texture type with creped surface which permits rapid filtration. The filtrate was used immediately for conductivity measurement by the instrument, being added to the test cell after the instrument was properly set, removed and added the second time to establish complete wetting of electrodes. A reading was obtained by manipulation of the selector switch and then the temperature of the filtrate was measured. The chart for conversion of meter readings to percent moisture was calibrated for a 29.4° C. (85° F.) temperature of the filtrate. After conversion, the results were corrected for temperature. In addition to a temperature correction, it was necessary to make a solvent correction. The solvent correction was a value obtained from a daily blank determination using a sample of the solvent, since moisture content may vary from day to day. The moisture content reported is the average of three determinations.

[b] The instructions for use of the Steinlite instrument contain tables of moisture values for corn which were determined by comparison with samples dried at 85 or 101° C. (185 or 214° F.) for 16 hours in an air oven. Duplicate determinations were made using 2-g. samples.

RESULTS

The mean moisture determinations with the three methods on 51 samples ranging from 62% to 79% moisture and taken from five varieties of sweet corn are given in Table 1. Each sample mean is the average of three determinations. The average percentage moisture of all samples was 70.4 with the vacuum oven, 70.0 with the Brown-Duvel tester and 70.5 with the Steinlite tester.

TABLE 1

Means of Triplicate Determinations of Moisture Content of Sweet Corn Using Five Varieties and Three Methods of Estimation.

Variety	Instrument		
	Vacuum oven	Brown-Duvel	Steinlite
Golden Cross	72.8	73.2	72.5
	72.5	67.8	71.4
	74.0	76.4	73.5
	70.5	69.8	70.8
	70.9	69.5	70.7
	67.9	68.1	68.4
	68.9	67.6	69.0
	67.9	66.2	67.5
	66.4	63.7	67.8
	66.7	65.8	68.3
	62.8	66.8	65.2
Golden Glory	71.0	71.2	72.4
	70.4	68.7	69.8
	69.2	68.3	69.6
	69.2	68.6	69.7
	67.6	67.5	68.7
	66.1	69.4	67.3
	65.8	66.2	66.2
	65.9	64.2	67.5
	65.1	65.0	66.8
	63.3	60.5	65.4
Tendermost	78.1	75.0	75.1
	78.5	77.5	77.6
	75.1	78.3	74.8
	74.6	75.2	74.2
	74.8	75.2	73.8
	72.5	71.0	71.0
	72.0	73.7	70.8
	72.5	71.9	71.9
	69.4	69.3	70.6
	69.9	69.6	68.9
	68.4	67.2	68.6
	67.4	67.0	68.7
Victory Golden	76.9	75.1	75.5
	77.3	77.6	75.7
	73.2	74.3	73.1
	71.7	68.6	71.5
	71.8	71.6	71.2
	68.7	69.6	69.2
	68.3	69.8	69.3
	66.2	65.4	67.9
Iochief	78.2	77.5	75.9
	77.3	75.4	75.1
	72.8	70.3	71.6
	72.7	70.8	72.4
	71.2	72.3	71.0
	68.4	68.4	69.2
	68.7	67.0	69.3
	67.2	67.2	67.1
	66.4	65.5	67.8
	66.4	66.4	67.4
Instrument Mean	70.4	70.0	70.5

For purposes of comparisons among the three methods, the vacuum oven is used as the standard. Analyses of variance of the differences in moisture determinations between the vacuum oven and the Brown-Duvel tester and between the vacuum oven and the Steinlite tester are given in Table 2. A test for the equivalence of two scales in measuring differences among treatments given by Cochran *(2)* is the ratio of the pooled mean square for varieties and mean and the

TABLE 2

Analyses of Variance of Determinations Between Means of Methods and Among Varieties

Source of Variation	Degrees of freedom	Vacuum oven-Brown-Duvel, Mean square	Vacuum oven-Steinlite, Mean square
Mean	1	10.645	0.201
Varieties	4	0.724	3.930
Error	46	2.975	1.215

mean square for error. This test indicates that the Brown-Duvel tester and the vacuum oven are equivalent in measuring the differences in moisture content among the varieties. The mean difference between the two methods is not quite significant at the 5% level as measured by the ratio of the mean square for mean and the mean square for error. Additional evidence based on the linear regression of the 51 mean determinations by the Brown-Duvel tester on those by the vacuum oven supports the conclusion that the two are equivalent in measuring the moisture percentage in sweet corn that has been frozen. This regression is $Y_1 = 3.3 + 0.95\ X$. If the two are equivalent the y-intercept should equal zero, the regression coefficient should equal one, and neither of the observed values in the above equation differs significantly from the expected.

The analysis of variance of the differences between the determinations made with the vacuum oven and the Steinlite indicates that the two methods are not equivalent and that they do not differ by a constant, although the means of all determinations by the two methods are almost identical. That the determinations are not the same on the individual samples for the two methods is also shown by the regression $Y_2 = 18.37 + 0.74\ X$. The value 18.37 differs significantly at the 1% level from zero, the regression coefficient differs significantly from one, and there is sufficient evidence to conclude that the regression is linear. The differences between the vacuum oven and Steinlite and between the vacuum oven and the Brown-Duvel are plotted against the determinations by the vacuum oven shown in Figures 1 and 2.

The scatter diagram shown in Figure 1 is a comparison of the results obtained with the vacuum oven with deviations of the Steinlite results from those of the vacuum oven. It should be apparent from this figure that use of the vacuum oven as a standard of comparison

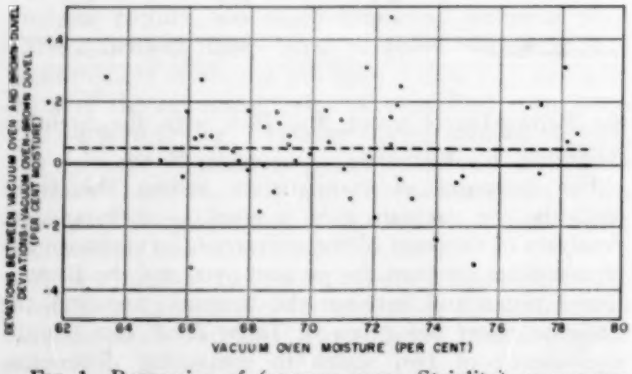


FIG. 1. Regression of (vacuum oven—Steinlite) on vacuum oven readings showing how the difference between the two methods varies over the range 62-78% moisture.

yields results which are not identical with those derived through use of the Steinlite instrument. Within the range of 68-73% moisture as determined by the vacuum oven, deviations are generally within 1%. When the range is extended to include 62-79% the deviations increase to approximately 3%.

A comparison of Figure 1 with Figure 2, indicates that the deviations of the Brown-Duvel determinations

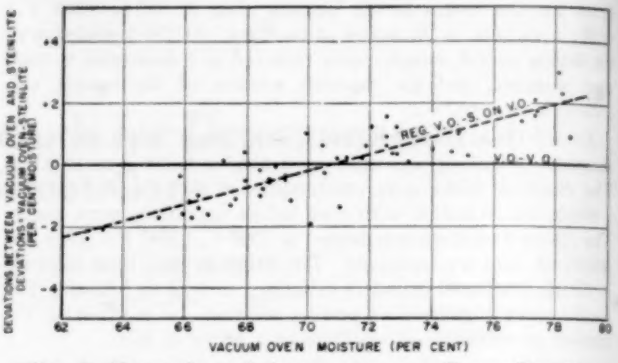


FIG. 2. Regression of (vacuum oven— Brown-Duvel) on vacuum oven showing wide variations between the two methods over the range from 62-78% moisture.

from those of the vacuum oven are consistently large over the entire moitsture range tested. This is illustrated again in the regression lines shown in Figures 3 and 4.

Actual corrections for either the Steinlite or the Brown-Duvel could be made from the regression lines (Figures 3 and 4) or perhaps more conveniently from a chart containing the same information.

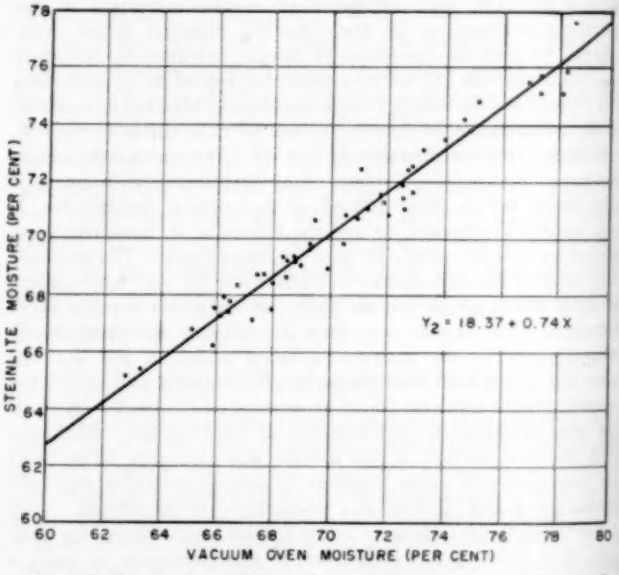


FIG. 3. Regression of Steinlite on vacuum oven moisture determinations.

The standard deviations were 0.39, 0.69 and 1.17% for the vacuum oven, Steinlite, and Brown-Duvel instruments (Table 3), indicating that the least average deviation from the mean would be expected through use of the vacuum oven. The standard deviation of the Steinlite instrument was approximately twice that of

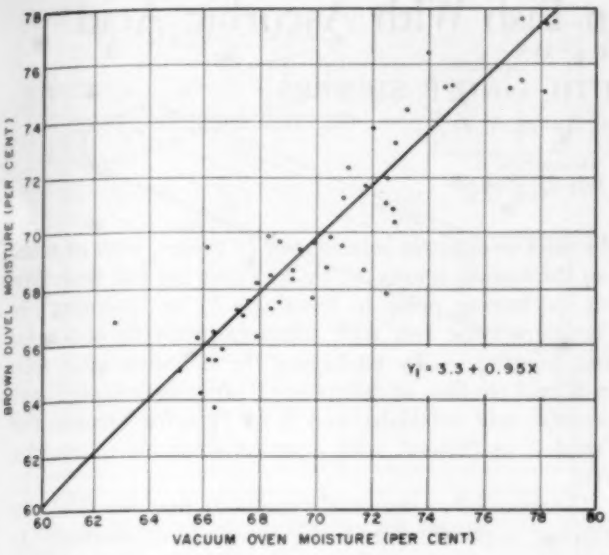


FIG. 4. Regression of Brown-Duvel on vacuum oven determinations.

the vacuum oven while the Brown-Duvel standard deviation was approximately three times that of the vacuum oven. The standard deviation 1.17% was the same as that obtained by Carter, Olson, and Henry *(1)*.

In terms of relative efficiency, assuming the vacuum oven to be 100%, the Steinlite was 32.3% as efficient and the Brown-Duvel only 11.0% as efficient as the vacuum oven. Efficiency may also be expressed in terms of its effect on sampling requirements. Three samples for the Steinlite and nine for the Brown-Duvel would be required to yield moisture values of approximately equivalent accuracy.

TABLE 3

Sampling and Operation Time Requirement For the Vacuum Oven, Steinlite and Brown-Duvel Methods

Comparative Expression	Instrument		
	Vacuum oven	Steinlite	Brown-Duvel
Mean Square Deviation (Variance)	0.15	0.47	1.36
Standard Deviation	0.39%	0.69%	1.17%
Relative Efficiency	100.0%	32.3%	11.0%
Number of determinations for equivalence	1	3	9
Time required to obtain equivalent accuracy by each method	5 hours	15 min.	5.25 hours
Time required for one determination	5 hours	5 min.	35 min.
Probable equivalent time under plant conditions	5 hours per 20 samples	5 hours per 60 samples	30 hrs. per 180 samples

Another factor of importance in evaluating efficiency is the time required to obtain results. If determinations were made one at a time, five hours would be required using the vacuum oven, 35 minutes with the Brown-Duvel, and only five minutes for each determination in the Steinlite instrument.

If the required times for determination of moisture are adjusted to include sufficient samples to provide a similar degree of accuracy in each case, the vacuum oven and the Brown-Duvel methods would require approximately five hours each while the Steinlite method would require only 15 minutes.

In a quality control operation it is usually desirable to operate instruments near their rated capacity. The ordinary vacuum oven will hold about 20 samples and a bank of six Brown-Duvel flasks will accommodate six samples simultaneously. The Steinlite instrument has a capacity of only one sample at one time. Taking these factors into account in addition to the sampling requirements for equivalent accuracy (Table 3), 20 samples could be run at one time in the vacuum oven in five hours. Sixty samples would be required if the Steinlite instrument were used, but the sixty samples could also be run in five hours. Using the Brown-Duvel, six-unit instrument, 180 samples and approximately 30 hours would be required.

Results from the Steinlite could be obtained at five minute intervals while those from the Brown-Duvel instrument would be available at approximately 35 minute intervals. The vacuum oven would provide results only after five or more hours.

SUMMARY

Comparisons of moisture content have been made on 51 samples of 5 varieties of sweet corn over the range of 62-79%.

The vacuum oven method was used as a standard and was compared with the Steinlite and the Brown-Duvel methods.

Three samples for the Steinlite and nine for the Brown-Duvel would be required to yield moisture values approximately equivalent to one vacuum oven sample.

Determinations of moisture content of frozen sweet corn samples made with the vacuum oven were found to vary less from their mean than those of the Steinlite and the Brown-Duvel.

Under laboratory conditions moisture estimates may be obtained in approximately 5 minutes using the Steinlite tester, 35 minutes using the Brown-Duvel instrument, and only after 5 or more hours with the vacuum oven.

LITERATURE CITED

1. CARTER, G. H., OLSON, O. E., AND HENRY, J. L. Which maturity index method best for raw sweet corn? *Food Packer*, **31** (9), 44 (1950).
2. COCHRAN, W. G. The comparison of different scales of measurement for experimental results. *Ann. Math. Stat.*, **14**, 205 (1943).
3. CULPEPPER, C. W., AND MAGOON, C. A. Studies upon the relative merits of sweet corn varieties for canning purposes and the relation of maturity of corn to the quality of the canned product. *J. Agr. Research*, **28**, 403 (1924).
4. HUELSEN, W. A., AND MICHAELS, W. H. The yield complex of sweet corn. Ill. Agr. Expt. Sta. *Bull.*, 432 (1937).
5. JENKINS, R. R., AND SAYRE, C. B. Chemical studies on the open-pollinated, top-cross and hybrid inbred strains of yellow sweet corn in relation to the quality of the canned product. *Food Research*, **1**, 199 (1936).
6. KRAMER, A., GUYER, R. B., AND IDE, L. E. Factors affecting the objective and organoleptic evaluation of quality in sweet corn. *Proc. Am. Soc. Hort. Sci.*, **54**, 342 (1949).
7. KRAMER, A., AND SMITH, H. R. The succulometer, an instrument for measuring the maturity of raw and canned whole kernel corn. *Canner*, **102** (24), 11 (1946).
8. PRATT, L. F. Moisture content as an indication of maturity in sweet corn. *Canner*, **88** (12), 80 (1939).

Commercial Processing of Frozen Fish With Ascorbic Acid[a]

J. C. BAUERNFEIND, E. G. SMITH, AND G. F. SIEMERS
Hoffmann-La Roche Inc., Nutley, N. J.

(Manuscript received July 25, 1950)

An applied study is made of methods of adding crystalline ascorbic acid to frozen cut fish as a means of retarding the development of oxidative rancidity during storage. Design of equipment and the application of the method to sea and lake fish are discussed.

Over the past five years a number of reports of basic research *(8, 9)* have appeared on the effectiveness of added ascorbic acid to fish fillets and steaks in retarding the development of rusting or yellowing and rancidity. With the retardation of these enzymatic oxidative changes, the frozen product is able to retain its fresh fish character for a longer period of time *(1, 2)*, assuming, of course, that top quality fish was processed initially and that the fish would be properly packaged and stored *(5)*.

The recently accepted principle of delaying the development of enzymatic oxidation and rancidity by the addition of a non-toxic chemical compound *(3)* naturally present in foods, seems to be a sound and practical approach. Because of the nature of fish itself and the processing steps involved, the use of a water-soluble compound is to be preferred.

Crystalline L-ascorbic acid, a water-soluble compound, is identical with natural ascorbic acid and is non-toxic. Treatment of the fish with this compound actually tends to increase the nutritive value of the fish, although no added value is claimed by the treatment. The effectiveness of ascorbic acid is believed to be due to its ability to unite easily with the oxygen of the air, thus preventing oxygen from initiating oxidative changes until the ascorbic acid content is exhausted around the critical areas of susceptible tissue. It therefore has a sparing action. Acidity measurements of ascorbic acid treated and control fillets have shown very slight changes in pH values. No important texture changes have been reported resulting from the ascorbic acid treatment.

Ascorbic acid in solution is not as stable as it is in dry form. If it were perfectly stable it would not have oxygen accepting or antioxidant value. Its destruction is accelerated by oxidative enzymes and the presence of small amounts of iron and copper in solution. It is recommended that the volume of aqueous solutions for dipping and spraying use remain small and that their preparation be made, where possible, on a daily basis. Dipping solutions should preferably be kept cool. Since fish preparation rooms are usually cool, this becomes practicable. Copper and iron containers should be avoided. Stainless steel, glass, aluminum, wood, or non-chipped porcelain enameled equipment is satisfactory.

Experimentally it has been demonstrated that ascorbic acid could be applied to the fish tissue: 1, by dipping the fillet in aqueous solutions or in brines, with or without thickening agents; 2, by spraying the fish flesh during packaging prior to freezing; 3, by "painting" or "brushing" the fish with solutions prior to packaging and freezing; 4, by packaging the individual fish fillet in films (pliofilm or cellophane) previously coated with ascorbic acid solutions, and 5, by "glazing" frozen fish "steaks" or "fillets" with aqueous solutions of ascorbic acid.

Commercially, two basic methods are practical, the dipping application and the spraying application. In both instances aqueous ascorbic acid solutions, with or without thickening agents can be employed. In applying ascorbic acid commercially to fish tissue it is basic to understand that the ascorbic acid method should in no way be regarded as a means to engage in poor processing practices, but should be regarded as a method to aid the retention of the fresh fish character for a longer storage period. Since fillets, steaks, and dressed fish from well washed fish under sanitary conditions will normally contain considerably fewer spoilage bacteria *(10)*, mechanical devices for washing fish thoroughly with clean water are recommended, prior to the ascorbic acid treatment.

From the mechanical viewpoint, for fish fillets weighing one-quarter to a pound or more and for gutted small fish weighing up to two pounds, it seemed desirable to use the endless belt principle to dip the units through an ascorbic acid solution. A tank holding a minimum volume of solution, yet large enough to permit a fairly rapid production rate was estimated to be satisfactory for commercial use. From observations of New England fisheries it was judged that a tank constructed to handle 500 pounds per hour would take care of the majority of the processors. In the small fisheries where production does not reach a figure of approximately 200 pounds per hour, it would seem more practical to use some method of hand dipping or to use a mechanical scoop dipping device, as suggested by the Pacific Fisheries Experimental Station *(4)*.

DESIGN AND CONSTRUCTION OF DIPPING TANK

The design of the Roche fish dipping tank is an adaptation[b] of small brining tanks, as illustrated in Figures 1 and 2, in use in many New England fisheries. It differs from the brining tanks in that it is narrower and that all possible dead space is eliminated below the moving belt so as to reduce the volume of ascorbic acid solution to the lowest possible amount. As built, the tank holds 12 gallons of solution when brim full. During operation, 8 to 10 gallons can be placed in the tank.

The moving belt (a LaPorte chain) used is a ½" flat mesh stainless steel belt 6" wide. The installation of ¾" stainless

[a] Presented before the Tenth Annual Meeting of the IFT, Chicago, Illinois, May 23, 1950.

[b] The plan was drawn by Mr. George Parman after consulting with several fish technologists. It was manufactured by the Universal Conveyor and Manufacturing Company of South Boston, Massachusetts.

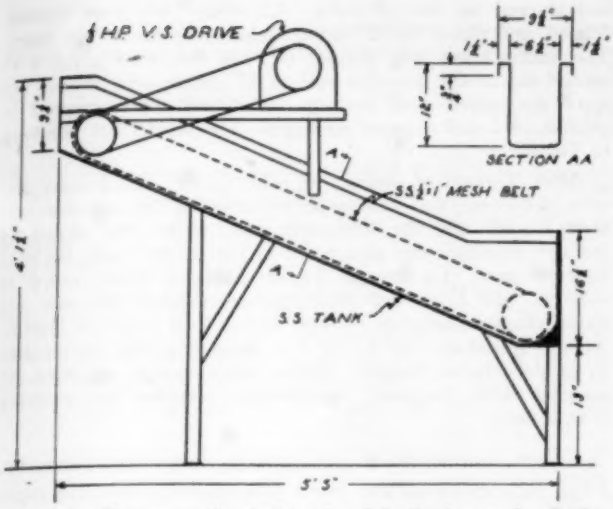


FIG. 1. Diagrammatic sketch of a fish dipping tank. Scale: 1" = 1'.

steel flight conveyers 8" apart on the belt were recommended following trial use. The belt runs on two 6" sprocket wheels, the submerged one is an idler, the exposed one, the driver. The driving sprocket is driven from a ¼ h.p. geared head motor at 9 r.p.m. giving a belt speed of about 14' per minute. This belt speed gives a dipping time of the individual fillet of approximately ten seconds. If the tank were redesigned it is suggested that the motor be located under the tank to make the belt more accessible. A drain plug should be located at the very bottom of the tank. Adjustable leg extensions permitting some variations of the slope of the belt were installed on the front set of legs. All metal parts in contact with the ascorbic acid solution are made of stainless steel.

FIG. 2. Full view of fish dipping tank demonstrating general construction and adjustable front legs.

PERFORMANCE OF THE DIPPING TANK

Data has been gathered as a result of a few commercial runs made on the Eastern Coast to enable a report to be made on the performance of the dipping tank. The tank had been designed so that it could receive the washed fish as they came off the conveyer from the cutting or brining tables. During the run an attempt was made to simulate as closely as possible the way the fish would normally come off the conveyer, that is, singly and in groups of 5 or 6 closely bunched. In feeding the fillets into the tank it was observed that there was no tendency for the fillets to cling together if several were added at one time. The flotation effect and slight stirring action of the belt kept the fillets in motion at all times, and all parts of the fillets came in contact with the ascorbic acid solution. The dipping operation did not impair the physical appearance of the fillets in any of the runs.

When the stainless steel belt is removed and the drain plug is open the tank can be cleaned with the aid of running water, a cleansing agent for stainless steel, and a few brushes. The use of steam or boiling water would further facilitate cleaning.

As the fish fillets pass through the ascorbic acid solution there is a gradual decrease in the volume of the dipping bath. The amount of solution taken up by the fish or fish fillet will, of course, depend on a number of factors *(1)*, but in any processing plant this decrease in dipping solution will follow a pattern.

TYPES OF DIPPING SOLUTIONS

Dipping solution may be prepared with *(7)* or without thickening agents. The concentration of ascorbic acid in the solution and the time of immersion are important factors. The major portion of the ascorbic acid uptake occurs during the first 10 or 20 seconds of immersion in aqueous solutions. Furthermore, the ascorbic acid uptake during this period of time is roughly proportional to the ascorbic acid concentration of the solution (at least for the concentration levels of 0.5 to 2.0%).

Since these aqueous solutions filter with relative ease and contain appreciable quantities of ascorbic acid, it is suggested that they be filtered at intervals depending on use. When the dipping of the fish begins, the ascorbic acid solution is clear, but when hundreds or thousands of pounds of fish fillets pass through the bath, the solution becomes very turbid. From the viewpoint of minimizing the bacterial count of the dipping solution, it would seem a wise practice to filter the solution following each run of 1,000 or 2,000 pounds of fish through the tank, or at least once a day, preferably at the end of the day when the filtered solution can be stored at refrigerator temperature, 4° C. (40° F.) overnight to be used again the following day. After treating 10,000 pounds of fish or after using for three or four days of operation (filtering and storing the solution properly), it is probably wise to discard the solution and start anew, unless the operator has laboratory facilities to check the bacterial and sanitary condition of the solution. Simple methods for estimating the ascorbic acid content of the solution and for ascorbic acid replacement have been worked out *(12)*.

Filtration of the ascorbic acid solutions extends their usefulness. For the filtering operation a source of vacuum is required. A large porcelain table filter accepting the 12-inch circular asbestos discs of varying degrees of retentiveness is satisfactory, In the filtration experiments it was found that the addition of 2 to 4% of a filter aid (Filter-Cel) to the solution prior to passing it through a coarse (Ertel No. 3) asbestos filter pad

brought about rapid clarification. Bacterial plate counts *(11)* before and after filtration demonstrate that 80% of the bacteria was retained in the sludge on the filter. Using a bacterial retentive pad (Ertel No. 0), a relatively bacterial free filtrate can be obtained, but the filtration rate is slow.

Aqueous ascorbic acid solutions containing fish soluble matter seem to be relatively stable. In a shad-dipping commercial run, the ascorbic acid content decreased during the operation (275 pound run) of the tank at 12° C (54° F.), from 1.53 to 1.48%. Stored at a temperature of 4° C. (40° F.) the content was the same 24 hours later, and another 24 hours later the content was 1.41%. The solution had not been filtered at any time. Some of the ascorbic acid solution from a mackerel run (1950 pounds) was stored at 4° C. (40° F.) in a large, partially filled glass container for 40 days, during which time the ascorbic acid content decreased from 1.6 to 1.3%.

DIPPING TRIALS WITH THE ROCHE TANK USING AN AQUEOUS SOLUTION OF ASCORBIC ACID

In a small commercial trial run on shad fillets, fish caught in the Hudson River, were boned, filleted, and iced in New York City and were sent to Poughkeepsie in metal containers. At the time of processing, the fish were of good quality according to odor and appearance observations. The fillets were given a water wash before dipping. The fillets were hand fed into the dipping tank which at the beginning contained 10 gallons of a 1.5% ascorbic acid solution (pH 3.3) made with tap water. The average dipping time for fillets to pass through the solution according to several timing trials was found to be 10 to 12 seconds. The individual fillets were then placed on waxed cardboard and covered with a pliofilm sheet which was then heat sealed to the cardboard. The results of the trial are summarized in Table 1.

After 4 months of storage at —18° C. (0° F.) differences between the packs were apparent as the untreated fish began to take on an off-odor. At the 12-month period the untreated fillets were rancid and yellow, while the treated fillets were not discolored and were judged as retaining good odor and flavor. After 24 months of storage a good color difference was still apparent, but the physical nature of both samples of fish was impaired.

Another trial was run on mackerel fillets. The fish were landed at Gloucester, Massachusetts and shipped to New Bedford under refrigeration. The fish were in good condition, firm, and showed no loss of color. All whole fish were cleaned, filleted, and placed in 12° brine (salometer) for 1 to 6 hours. The excess brine was drained off, and fish were given a 10 second dip in 2% ascorbic acid in 12° brine. All treated fish were discharged onto packing tables and were wrapped in pliofilm in 1 and 5 pound packages. The results are presented in Table 2.

After 2 years of storage at —18° C. (0° F.), a color and odor difference was still apparent between the ascorbic acid treated pack and the untreated pack. After this period of storage, rancidity was also noted in the treated pack, but to a lesser degree. Usually in frozen mackerel fillets stored at —12° C. (10° F.) initial rancidity, as evidenced by odor and flavor changes, becomes evident after 6 to 8 weeks of storage, while if stored at —18° C. (0° F.), about 4 months are required to produce these changes. Under either storage condition the ascorbic acid treatment significantly retarded the rancidity development.

Other commercial dipping trials have also been run. Cost figures resulting from the various dipping trials with aqueous solutions where mechanical dipping was employed show a range of 0.39 to 0.64 cents per pound of fillet. This range of cost figures based on short trials is due to small volume runs and the occasional lack of desirable facilities. These costs are based on the amount of ascorbic acid used during the processing. Presumably, that which remains in the solution at the end of the day will be used in further dipping runs. If discarded, the costs would be increased.

For costs of operation in the hand dipping of fish with aqueous solutions we turn to data of the Pacific Fisheries Experimental Station on the dipping of Coho Salmon steaks. In all, 1,000 pounds of steaks were treated, and the ascorbic acid content of the solution (a volume of 6 quarts) ranged from 0.80 to 1.33%. The salmon steaks (about ¾" thick) were first washed in water, then immersed in this solution. The steaks were cellophane-wrapped and placed in five pound packages and frozen. Of the 220 g. of ascorbic acid used for the test 53 g. remained in the dipping solution. Based on ascorbic acid content of the steaks, a total of 167 g. of the crystalline ascorbic acid was used, which would cost 0.42 cents per pound of fillet. In another study on 660 pounds of sole fillets, using a 1.5% solution of ascorbic acid, the cost based on the ascorbic acid used was 0.53 cents per pound of fillet. With small quantities (1,500 pounds or less) of fillets, it may be more economical to hand dip than to use the tank since one can control the

TABLE 1

Ascorbic Acid Treatment of Shad Fillets for Freezing

Period No.	Time	Dipping Solution			Fish Fillet			
		Volume	Temp.	Ascorbic Acid [a]	Weight Processed	Ascorbic Acid	Total Vitamin C. [d]	Bacteria [e]
		gallons	*°F.*	*%*	*lb.*	*mg./lb.*	*mg./lb.*	*per g.*
Control	.....	.....	.....	.....	.....	.....	.....	650,000
1	10:50 A.M.	10	55	1.53	.....	202	231	295,000
2	11:15	.....	.....	1.52	.....	192	210	343,000
3	11:30	.....	54	1.51	.....	222	248	333,000
Shutdown								
4	1:55 P.M.	.....	.....	1.50	.....	107	116	360,000
5	2:15	.....	.....	1.50	.....	244	274	151,000
6	2:30	.....	53	1.49	.....	205	229	513,000
7	3:00	9	.....	1.48	275	105	124	225,000
Average of Treated Fish	.....	.....	.....	.....	.....	183	204	317,000

[a] As determined by iodine titration. [d] Total vitamin C is the combined reduced ascorbic acid and dehydroascorbic acid as determined by the photoelectric dichlorobenzenoneindophenol method after hydrogen sulfide reduction; ascorbic acid or reduced ascorbic acid is determined by the same method before reduction. Both reduced ascorbic acid and dehydroascorbic acid are biologically active forms of vitamin C. [e] As determined by bacterial culture plate method.

TABLE 2

Prefreezing Ascorbic Acid Treatment of Mackerel Fillets for Freezing

Period No.	Time	Dipping Solution				Fish Fillet			
		Volume	Temp.	Ascorbic Acid	Bacteria	Weight Processed	Ascorbic Acid	Total Vitamin C	Bacteria
		gallons	*°F.*	*%*	*per ml.*	*lb.*	*mg./lb.*	*mg./lb.*	*per g.*
1	9:20 A.M.	12	46	1.9	.....	.....	113	154	138,000
2	9:35	12	48	1.9	2,750,000	50	154	180	62,000
3	9:50	12	48	1.9		150	.....	.....	310,000
4	10:10	11	49	1.9	2,500,000	250	151	188	150,000
Shutdown									
5	11:05	11 [f]	.....	1.8	1,700,000	450	170	234	240,000
6	11:10	12	.....	2.1	.....	.....	.....	.....	.....
7	11:30	12	.....	2.0	7,000,000	650	.....	.....	100,000
Shutdown									
8	2:00 P.M.	12	48	2.0	.....	850	157	214	.....
9	2:30	12 [g]	48	1.8	.....	1050	.....	.....	.....
10	3:00	12	.....	2.0	6,000,000	1250	.....	.....	30,000
11	3:30	12 [h]	.....	1.9	.....	1450	.....	.....	.....
12	4:00	12	48	1.9	5,000,000	1650	139	170	60,000
13	4:30	12	.....	1.8	.....	1850	.....	.....	.....
14	4:50	12	48	1.6	5,000,000	1950	189	234	120,000
Average of Treated Fish		.....	.....	.....	.....	.....	153	196	134,444

Crystalline ascorbic acid added: [f] 6 oz., [g] 5 oz., [h] 2 oz. in aqueous solution.

volume of solution so that only a small volume remains at the end of the processing period.

DIPPING SOLUTIONS WITH THICKENERS

As has been stated, the dipping technic may be varied by adding thickening agents to the solution. When this is done the solution becomes more viscous and more adheres to the fish tissue. Lower concentrations of ascorbic acid can therefore be used, varying from 0.25 to 1.0%, to obtain the same ascorbic acid content on the fillet as compared to aqueous solutions containing only ascorbic acid in the range of 0.5 to 2.0%.

Several thickening agents have been used experimentally and commercially in the following concentrations in water solution: Sodium carboxymethylcellulose (CMC), low viscosity, 2.0-3.5%; Sodium carboxymethylcellulose (CMC), high viscosity, 0.3-0.5%; Methyl cellulose (Methocel), 100 cps., 1.0-2.0%, and Irish moss extractive (Krim-Ko-Gel), high viscosity, 0.3-0.8%.

Sodium carboxymethylcellulose, a cellulose gum, is an odorless and tasteless granular white powder. The food-grade type is physiologically inert and is suitable for incorporation into food and pharmaceutitcal preparations. Methyl cellulose, a white fibrous product, is odorless and practically tasteless. Feeding experiments by independent laboratories have shown it to be non-toxic and relatively inert. Irish moss extractives (Krim-Ko-Gel, Kraystay), are derivatives of the well known Irish moss, and contain the active principle, gelose. Krim-Ko-Gel is a light tan-colored, flaky product and is used in various food and pharmaceutical products. The characteristics of these thickeners as listed above are based on the manufacturers' literature.

When thickening agents are used in appreciable quantities with low concentrations of ascorbic acid it is not recommended that these solutions be filtered. Preferably, these viscous solutions should be used up by the end of the day's run or applied until the minimum required volume of solution is reached and the remainder be discarded. If several thousand pounds of fish are to be processed during the day, it is wise to repeat this procedure several times as a sanitary precaution.

The following experiment demonstrates the difference in ascorbic acid pick-up of fillet dipped in ascorbic acid solutions with and without thickening agents. Fresh mackerel fillets were cut in the morning and within a few hours were washed, dipped in solutions of ascorbic acid for 20 seconds at 22° C. (72° F.), individually packed in pliofilm, and frozen, at —34° C. (—30° F.). The frozen fillets were assayed for ascorbic acid by the photoelectric method *(6)*. The variables used in the test and the results are presented in Table 3. When thickening agents were present in the dipping solutions the fillets adsorbed two to three times the amount of ascorbic acid as compared to fillets dipped in the same solutions without thickening agents. At the lower temperatures of the commercial fish rooms where the thickened solution would become more viscous, the fillets may take up a greater quantity of ascorbic acid.

TABLE 3

Uptake of Ascorbic Acid by Mackerel Fillets During Dipping (20 seconds at 72° F.)

Aqueous Dipping Solutions	Total Vitamin C Content [1]	
	Single values	Average
	mg./lb.	*mg./lb.*
Water	7	7
0.5% ascorbic acid	58, 41	50
1.0% ascorbic acid	97, 119	108
0.5% ascorbic acid plus 0.5% Krim-Ko-Gel	118, 116	117
0.5% ascorbic acid plus 0.75% Krim-Ko-Gel	142, 134	138
0.5% ascorbic acid plus 0.3% C. M. C.	104, 115	110
0.5% ascorbic acid plus 0.5% C. M. C.	95, 153	124

[1] Combined reduced ascorbic acid and dehydroascorbic acid content. See footnote [4], Table 1.

TREATMENT OF LARGE, GUTTED FISH BY SPRAY APPLICATIONS

Difficulty was expected when large, gutted fish weighing five to one hundred pounds were to be treated with ascorbic acid if the dipping technics were the only method of application. It was therefore desirable to examine spray applications.

First, the stability of ascorbic acid in a water spray as well as in thickened water sprays was tested. A spray gun in which all parts were made of stainless steel or aluminum was applied. The Eclipse Unit, Model G-6P gun, is normally manufactured with one part, the fluid post for cup assembly, made of brass. The gun was held 6" from the object and was operated at a pressure of 10 p.s.i.g. Since it may be desirable to have a solution more viscous than water to decrease the run-off or drip following the spraying of gutted fresh fish, thickening agents may be added to the aqueous solutions. The solutions were made up shortly before the spraying operation. The thickeners were dissolved in tap water before the ascorbic acid was added. The solutions were sprayed against a piece of cellophane, and the drip therefrom collected for respraying. A second series was set up to again test the effect of multiple spraying. Ascorbic acid was determined by titration with a standard iodine solution. The results are recorded in Table 4.

TABLE 4

Stability of Ascorbic Acid in Aqueous Sprays

Description	Ascorbic Acid Content		
	Initial solution	After first spray	After second spray [1]
	%	%	%
1% ascorbic acid, 3% sodium carboxymethylcellulose solution	0.94	0.95	0.99
1% ascorbic acid, 1.5% methocel solution (A)	0.89	0.89	.....
1% ascorbic acid and 1.5% methocel solution (B)	1.01	1.03	1.03
1% ascorbic acid in water	0.93	0.98	.....

[1] Sprayed through the gun a second time. The ascorbic acid content of the 1% ascorbic acid and 1.5% methocel solution was 1.03% even after the third spraying.

These trials demonstrated that ascorbic acid is stable in aqueous solution following single or multiple low-pressure spraying. Ascorbic acid solutions used for spraying will, of course, be subjected to the same care of preparation given to dipping solutions, namely: preparation shortly before use, with out heat, and in suitable equipment. The cost of the spraying technic should be as economical as dipping or even more so since, by proper planning, no solution will remain to be discarded. Since ascorbic acid solutions are stable during the spraying operation, the cost of treatment during commercial application will rest entirely on the amount of ascorbic acid applied to the fish tissue, providing that spraying losses are controlled.

In spraying gutted fresh fish, care must be exercised not to rub the coating off in placing the fish in the freezer. Thickened solutions of ascorbic acid in this application appear to be better than aqueous solutions. Following freezing, the fish must be sprayed with water at intervals to maintain an ice glaze to protect the fish from dehydration if it is not wrapped in moisture-vapor-proof films.

In spraying frozen gutted large fish (glazing following freezing) water solutions of ascorbic acid will probably be satisfactory as the spray quickly freezes on the surface of the fish and provides a protective layer. At least 100 mg. of ascorbic acid (range 100-200 mg.) should be used per pound of fish which is supplied by one-sixth fluid ounce of a 2% ascorbic acid solution or one-third of a fluid ounce of a 1% solution per pound of fish. As already stated, plain water glazes can be applied at intervals to the fish to prevent loss of the ascorbic acid glaze, if the whole gutted fish is to be held for an extended period.

SPRAYING AND GLAZING TRIALS ON SALMON

In order to test the effectiveness of the spray method during plant operation, a small commercial run was arranged on the West Coast. During this test the glazing of frozen salmon steaks and the dipping of salmon fillets were also observed.

With the cooperation of the Fishermen's Co-operative Federation, Vancouver, B. C. a fairly extensive experiment was set up testing the ascorbic acid treatment of whole dressed (gutted and head removed) salmon, salmon steaks, and salmon fillets.

The trials were conducted on Red King (Spring Canadian), Silver (Coho Canadian), Pink (Pink Canadian), and Bright Fall (Silver Bright Canadian) salmon during the early fall of 1948. The dressed salmon were treated either with a spray of a water, an aqueous 2% ascorbic acid solution, or an aqueous 2% ascorbic acid, 0.4% sodium carboxymethylcellulose (CMC) solution, then frozen and water glazed. In other experiments frozen steaks sawed from freshly frozen Red King, Silver, and Bright Fall dressed salmon were either water glazed, glazed with a 1% ascorbic acid solution, or with 1% ascorbic acid, 0.4% CMC solution before packaging. In another trial Bright Fall fillets were either water dipped or dipped in a 2% aqueous ascorbic acid solution for ten seconds prior to packaging and freezing.

The dressed salmon were judged by examining the condition of raw and cooked steaks cut from these fish. Examination of the dressed Red King salmon sprayed with water (control) revealed bleaching and development of slight rancidity after 5 months of storage at —18° C. (0° F.). These changes progressed, becoming quite pronounced at 8 months, and totally unacceptable in flavor as judged by cooked samples at the end of 16 months of storage. Dressed salmon treated with the ascorbic acid or ascorbic acid-CMC spray possessed good color and flavor after 5 and 8 months but began to show slight rancidity after 16 months of storage. Those treated with the ascorbic acid-gum spray were slightly superior. Changes in the Silver dressed salmon progressed more slowly, the control becoming very slightly rancid after 8 months of storage but quite definitely rancid after 16 months of storage. Both treated Silver lots displayed equally good color and flavor after 16 months of storage. Observations after 2 years of storage of both Red King and Silver dressed salmon still demonstrated wide flavor and odor differences between the control and treated lots, however, some bleaching and off-flavor development had started in the treated lots. The Bright Fall control dressed salmon showed slight rancidity, the Pink control dressed salmon appreciable bleaching and rancidity, after 5 months of storage. Both ascorbic acid treated lots possessed good color and flavor for the Bright Fall group. The treated Pinks were likewise superior, the ascorbic acid-CMC lot being slightly superior to the plain ascorbic acid lot. After 16 months of storage a marked difference existed between the Bright Fall groups, controls displaying rancid color and odor, the treated no yellowing and superior flavor. The Pink control salmon were very rancid and yellow, while the treated salmon showed slight rancidity and yellowing at the 16 month storage period.

The glazed frozen steaks were judged in the raw and cooked conditions. Steaks were cooked covered with water without seasoning in individual pans. After 6 months of storage cooked treated Red King, Silver, and Bright Fall steaks were preferred in taste panel trials to the control steaks. The greatest difference was noted in the Bright Fall group. The taste differences widened in the Red King and Silver lots at the twelve and sixteen month tasting periods. There was no appreciable difference between lots treated with ascorbic acid or the ascorbic acid-CMC solutions. As usual, bleaching was noted as correlated with the development of rancidity. At the 16 month storage period all steaks developed a noticeable toughening, probably associated with protein denaturation.

After 5 months of storage there were significant differences between the Bright Fall control fillets and the treated fillets, the latter possessing good color and flavor, the control a tan discoloration (rusting) and rancid odor.

GLAZING TRIALS

The ice glaze formed by coating frozen fish with cold water has been in general use by the industry for many years, principally on round and dressed fish. By using cold ascorbic acid solutions in place of water and controlling the weight of the glaze, the fish tissue can be coated by an ascorbic acid-ice layer. Since this glaze will evaporate during frozen storage, the steaked, filleted or dressed fish must be protected by a moisture-vapor-proof package, while large whole fish are given additional glazes of plain water when necessary. Several glazing trials are reported here.

In an eastern fish processing plant, whole salmon, Chinook or King, caught on the West Coast, beheaded, gutted, then frozen and shipped, were cut by bandsaw into steaks and dipped into water or an ascorbic acid solution. The control and treated steaks were packaged in pliofilm and stored at —18° C. (0° F.) for a 12-month period. At the end of 3 months there were no differences, but at the 5, 7, and 12 month examination periods

the treated samples retained their red color and flavor. The control samples became progressively poorer by bleaching and developing greater rancidity. An ascorbic acid analysis at the end of the 2 month period demonstrated the presence of 108 mg. of ascorbic acid per pound.

Swordfish were also treated in this plant in a similar fashion. The history and age of the dressed swordfish were unknown. At 3 and 4 months after treatment differences between the two packs appeared in color and flavor; the ascorbic acid treatment better retained the initial quality of the product. After 12 months of storage the water-glazed swordfish contained 0 and 4 mg. per pound of ascorbic acid and total vitamin C, respectively. These terms are used here with the meaning as given in footnote [d] in Table 1. After 2 and 12 months of storage the ascorbic acid-glazed swordfish contained 128 and 82 mg. per pound of ascorbic acid and 193 and 112 mg. per pound of total vitamin C, respectively.

While the development of rancidity can be delayed in mackerel fillets, no trials had been conducted on whole mackerel or mackerel in the round. The practice of treating whole mackerel commercially at this stage of knowledge is open to debate; it was, nevertheless, of value to learn whether it could be done experimentally.

Fresh whole mackerel from the New York wharf were secured, part of which were used in a dipping test. In the dipping trial one lot of fish was soaked in a 2% ascorbic acid aqueous solution for 5 minutes. Another lot was punctured (48 ⅛ inch skin punctures along the back and sides, avoiding the body cavity and head), and were likewise soaked for 5 minutes in the same solution. The fish were drained, frozen, and stored, packed in pliofilm, at —18° C. (0° F.). The second lot of the whole mackerel was frozen at —36° C. (—35° F.) and glazed until a weight increase of 5-6% was obtained (3 dippings). Different lots were glazed in water, an aqueous 0.5% ascorbic acid solution, and an aqueous 1.0% ascorbic acid solution. All fish were then sealed in pliofilm and stored at —18° C. (0° F.).

The results of this trial indicate that the ascorbic acid glazing trial was much more effective than the dipping variations. It is also a more practical approach to such a problem. After 18 months of storage at —18° C. (0° F.) the water-glazed whole mackerel was found to be quite rancid in flavor and odor. Similar fish glazed with either aqueous 0.5% or aqueous 1.0% ascorbic acid solutions possessed good flavor and odor. The glaze was protected during this storage period by pliofilm.

ASCORBIC ACID TREATMENT OF LAKE FISH

Arrangements were made with cooperating fish processors in the Great Lakes area for experimental trials on the ascorbic acid treatment of lake trout, white fish, and lake herring. In normal practice considerable amounts of these fish are frozen and stored. Dressed lake trout, white fish, and herring were gutted and dipped in aqueous solutions of ascorbic acid. From other trout and white fish, fillets were cut and likewise treated with the dipping solutions, water, an aqueous 1% ascorbic acid solution, and an aqueous 2% ascorbic acid solution for a 10 second interval. Following the above described treatments all fish were frozen.

A few samples were shipped to New Jersey for examination, and the remainder of the fish were placed in storage at —18° C. (0° F.) at the processing plant. The samples enroute to New Jersey became partially thawed, but were refrozen when received and examined 6 weeks after packing. Spectacular differences were noted in the lake trout fillets and to a lesser extent in the white fish fillets. The treated products were superior in color and flavor. Fish fillets not shipped but held frozen under ideal conditions in the lake area required many more months to show a similar contrast. After 15 months of storage in the midwest the fish processors reported that the control fish fillets possessed a much stronger fishy taste than the treated lots. No difference was noted between the lots treated with the 1 and 2% ascorbic acid solutions. These treated fish had, in their opinion, as good a flavor as such fish would normally have immediately after being frozen.

The dressed fish treated in the lake area and shipped east were examined after 5 months of storage in the raw condition as well as following cooking in individual pans under water without salt. The dressed lake trout and white fish dipped in 2% ascorbic acid for a 10 second interval were markedly superior in flavor to similar fish dipped in water. The treated lake trout possessed more pink color. Those dipped in 1% ascorbic acid for the same time interval were intermediate in quality. Little difference in color was noted in the herring packs, but flavor studies showed both treated lots to be superior to the control lot where slight rancidity had already developed. Greater differences between the control and treated herring lots were present after 12 months of storage.

BEHAVIOR OF ASCORBIC ACID IN STORED AND COOKED FISH

Ascorbic acid is not added to fish products because of its added nutritional value. Variability in content alone would preclude any nutritional claim, as would the loss in vitamin potency encountered following cooking. Furthermore, fish is not usually regarded as a source of vitamin C, in the minds of nutritionists and the public.

While ascorbic acid introduced in or around the frozen fish tissue retards the rancidification of the fatty tissue, it itself is slowly oxidized as the storage time progresses. A limited trial on mackerel fillets demonstrated this effect. Freshly cut fillets weighing 130 to 400 g. were dipped in ascorbic acid solutions, packaged, and frozen. After 3, 6, and 9 months of storage three individual fillets were assayed for ascorbic acid *(6)*. The results are recorded in Table 5. There is some variability in the ascorbic acid content of the fish fillet following treatment, probably due to the nature of the product itself, as well as to slight variations in the handling and packaging of the product. Salt added to frozen fish by heavy brining is known to accelerate the development of rancidity *(11)*. Observations in practical trials indicate that under these conditions more ascorbic acid is required for retarding rancidity.

Most of the ascorbic acid remaining in the fish at the end of the storage period is destroyed during cooking period. Trials with fish cooked in boiling water or broiled have shown that 70-80% of the ascorbic acid present in the raw state is destroyed as a result of the cooking treatment.

TABLE 5

Ascorbic Acid Stability[k] in Frozen Treated Mackerel Fillets

Treatment	3 Months Storage		6 Months Storage		9 Months Storage	
	Ascorbic acid	Total Vitamin C	Ascorbic acid	Total Vitamin C	Ascorbic acid	Total Vitamin C
	mg./lb. of fillet	*mg./lb. of fillet*	*mg./lb. of fillet*	*mg./lb. of fillet*	*mg./lb. of fillet*	*mg./lb. of fillet*
Control, water dip	.....	.....	0	7	2	4
	.....	.....	3	5	.....	.....
20 Second dip in 1% ascorbic acid water solution	154	164	119	141	87	101
	137	150	68	94	94	110
	128	133	68	90	104	120
Average:	140	149	85	108	95	110
20 Second dip in 1% ascorbic acid in 20° brine	136	151	81	105	100	105
	98	115	67	87	63	74
	122	132	73	88	74	84
Average:	119	133	74	93	79	88

[k] See footnote [4], Table 1 for an explanation of the terms used.

Appropriate labeling of the frozen fish package to show that ascorbic acid has been added is necessary under the Federal Food and Drug Administration regulations.

DISCUSSION AND SUMMARY

Commercially, two basic methods of ascorbic acid treatment are practical, the dip application and the spray application. In both applications aqueous ascorbic acid solutions, with or without thickening agents, may be employed. If aqueous solutions are employed in the dipping method, a concentration of ascorbic acid of 0.5 to 2% of the solution should be used. If thickened solutions are used, an ascorbic acid concentration of 0.25 to 1% is satisfactory since during the dipping operation more of this viscous solution adheres to the fish tissues. Carboxymethylcellulose, methyl cellulose, and Irish moss extractives have been used as thickening agents in commercial or experimental trials. When aqueous solutions of ascorbic acid are used it is recommended that an occasional filtration be employed to remove the sludge from the solution and to minimize bacterial content. Filtration methods are not practical with thickened solutions and therefore frequent replacement of the solution is recommended to maintain sanitary control.

A stainless steel tank for mechanically dipping 500 pounds of fish fillets or steaks per hour was developed. An endless belt is used to move the fish through the solution in ten seconds. Commercial trials with the dipping tank have been run which demonstrate that this processing method can be easily used in commercial fish processing lines as presently designed and operated.

In treating large, dressed fish with ascorbic acid, a spray technic is recommended using a conventional spray gun operated under low pressure. All parts touching the ascorbic acid solution should be made of aluminum or stainless steel. Ascorbic acid solutions with or without thickeners are stable during the spraying operation. Thickened solutions of ascorbic acid may be used for unfrozen large dressed fish, while an aqueous solution of ascorbic acid is satisfactory for large fish already frozen, as the spray quickly freezes to the surface of the frozen fish to provide a protecting glaze. At least 100 mg. of ascorbic acid (range 100-200 mg.) should be used per pound of fish.

Commercial trials on dressed salmon, salmon steaks, and salmon fillets as well as on mackerel fillets have well demonstrated the effect of ascorbic acid in retarding deteriorative changes previously assumed to be normal. Trials with fresh water fish such as Lake Trout, White Fish, and Lake Herring have given excellent results, thus demonstrating that the ascorbic acid treatment is not limited to ocean fish.

LITERATURE CITED

1. Bauernfeind, J. C., Smith, E. G., Batcher, Olive, and Siemers, G. F. Retardation of rancidity in frozen fish by ascorbic acid. *Quick Frozen Foods*, **10**, (8) 139; **10**, (9) 68 (1948).
2. DuBois, C. W. Ascorbic acid and color in food products. *Food Technol.*, **3**, 119 (1949).
3. Dunn, C. G. Chemical agents give quality improvements in fisheries. *Food Technol.*, **1**, 371 (1947).
4. Lantz, A. W. An apparatus for dipping fish fillets or steaks. Fisheries Research Board Can. Progress Repts., No. **82**, 6 (1950).
5. Lemon, J. M. Problems of preparing frozen packaged fish. *Frozen Food Industry*, **4**, (5) 18 (1948).
6. Rubin, S. H., Jahns, F. W., and Bauernfeind, J. C. Determination of vitamin C in fruit products. *Fruit Products J.*, **24**, 327 (1945).
7. Stoloff, L. S., Punocher, J. F., and Crowther, H. C. Curb mackerel fillet rancidity. *Food Inds.*, **20**, 1130 (1948).
8. Tarr, H. L. A. Control of rancidity in fish flesh I. Chemical antioxidants. *J. Fisheries Research Board Can.*, **7**, 137 (1947).
9. Tarr, H. L. A. Control of rancidity in fish flesh II. Physical and chemical methods. *J. Fisheries Research Board Can.*, **7**, 5 (1948).
10. Tarr, H. L. A., and Lantz, A. W. The effect of mechanical washing of fish on the keeping quality of fillets prepared from them. *Fisheries Research Board Can. Progress Repts.*, **81**, 80 (1949).
11. Tressler, D. K., and Evers, C. F. The Freezing Preservation of Foods. 1947, Avi Publishing Co., New York, N. Y.
12. Vitamin Division Release. Plant Control Procedure for Ascorbic Acid Solutions Used in Fish Dipping Trials. Hoffmann-La Roche Inc., Nutley, N. J.

Heat Transfer in Commercial Glass Containers During Thermal Processing. II. F_o Distribution in Foods Heating by Convection[a]

I. S. FAGERSON, W. B. ESSELEN, JR., AND J. L. LICCIARDELLO[b]
Department of Food Technology, University of Massachusetts, Amherst, Massachusetts

(Manuscript received December 22, 1950)

Studies on F_o distribution in glass containers have been extended to three foodstuffs, diced carrots, cut green beans, and apple juice which exhibit convection type heating. Although off-center minimal F_o values are found, their magnitude is less than that observed in 1% bentonite and in the foods studied are not less than 96% of the process value calculated for the conventional cold point.

In a previous study *(1)* of heat transfer in glass containers utilizing 1% bentonite suspensions as a means of obtaining convection type heating, it was reported that minimal F_o values did not occur on the vertical axis of the container, but are located between the axis and the jar wall. In view of the fact that the determination of the cold point in a container is generally based on the assumption that minimal F_o values are found on the vertical axis, it seemed desirable to determine the significance of off-center minimal process values in actual foodstuffs which exhibit convection type heating. Accordingly, heat penetration studies were made on three such types of food products, namely, cut green beans, diced carrots, and apple juice.

METHODS AND APPARATUS

The glass containers used were the No. 2½ size (401 x 414) fitted with vacuum type caps. The techniques used in obtaining the heat penetration data and calculating F_o values were essentially those previously described *(1, 2)*.

Fresh green beans were washed, trimmed, and cut into approximately 1½ inch lengths. They were then blanched in boiling water for approximately 2 minutes. After blanching the beans were immediately cooled in water and packed into the containers. The fill-in-weights were 16 ounces. About 5 grams of salt was added to each jar the jars being then filled with hot water leaving a headspace of ½ inch.

Fresh carrots were washed, trimmed, and diced in a manual dicing machine which produced cubes approximately ½ inch on a side. The fill-in-weights were 17½ ounces. Approximately 5 grams of salt was added to each jar and the containers were filled with hot water leaving a ½ inch headspace.

The apple juice used in these experiments was unclarified and was prepared from apples in the usual manner by means of a cider press. The juice was held in frozen storage at —17.8° C. (0° F.) prior to use. When thawed, it was heated to 60° C. (140° F.) and filled into the containers leaving a ½ inch headspace.

The initial temperature for all products was $60 \pm 1.1°$ C. ($140 \pm 2°$ F.).

For each product four processing runs were made to determine the location on the vertical axis where F_o values were at a minimum (the conventional cold point). Subsequent heat penetration studies were made with thermocouples located in a horizontal plane passing through this point. The thermocouples were located as shown in Table 1.

TABLE 1

F_o Distribution in No. 2½ Size Jars of Various Foods Processed at 115.6° C. (240° F.)[c]

Food processed	Run No.		Location of thermocouples, distance from jar wall in inches[d]		
			2	1¼	¾
Diced carrots	Jar A	1	8.00	8.13	7.85
		2	8.00	7.70	8.30
		3	8.00	8.20	8.40
Diced carrots	Jar B	1	8.00	8.05	8.30
		2	8.00	8.10	8.10
		3	8.00	7.70	8.10
			Ave. 8.00	7.98	8.18
Cut green beans	Jar A	1	8.00	7.83	8.08
		2	8.00	7.94	8.36
		3	8.00	7.84	8.52
Cut green beans	Jar B	1	8.00	7.67	8.29
		2	8.00	7.92	8.09
		3	8.00	7.78	7.66
			Ave. 8.00	7.83	8.16
Apple juice	Jar A	1	8.00	8.14	8.06
		2	8.00	8.01	8.11
		3	8.00	8.45	8.44
Apple juice	Jar B	1	8.00	8.02	8.04
		2	8.00	8.03	8.01
		3	8.00	8.09	7.98
			Ave. 8.00	8.12	8.11

[c] Initial temperature $60 \pm 1.1°$ C. ($140 \pm 2°$ F.).
[d] Thermocouples located in a horizontal plane ¾ of an inch from bottom of jar.

From the heat penetration data obtained, a process was calculated, using the general (graphical) method, to yield an arbitrary F_o value of 8.00 at the conventional cold point. F_o values attained at the other thermocouple locations for this process time were then calculated.

RESULTS

The F_o distribution in the three products studied are shown in Table 1. Off-center minimal values occurred rather frequently in both carrots and green beans, but in only one determination in apple juice. Off-center minimal values were usually found at points 1¼ inches from the jar wall whereas in 1% bentonite suspensions these minimal values were found ¾ of an inch from the jar wall. In diced carrots the range of F_o values found was from 7.70 to 8.40, in green beans from 7.66 to 8.52, and in apple juice from 7.98 to 8.45. Off-center minimal values were noted most frequently in green beans. In all cases the subminimal F_o values were not less than 96% of the calculated minimum values.

CONCLUSIONS

Although minimal F_o values were obtained at points between the conventional cold point on the vertical axis and the jar wall, the magnitude of these values indicate that the effect is much less pronounced in foodstuffs than in 1% bentonite suspensions. In apple juice the

[a] Contribution No. 789, Massachusetts Agricultural Experiment Station.
[b] Present address: Maine Agricultural Experiment Station, Orono, Maine.

effect was almost completely absent. The maximum effect was noted in one run of green beans where a point ¾ of an inch from the jar wall received 96% of the desired calculated lethality. Although non-symmetrical F_o distribution apparently occurs in foods heating by convection, in the foods studied it appears to have at most only a small effect on the calculated process value.

LITERATURE CITED

1. Fagerson, I. S., and Esselen Jr., W. B. Heat transfer in commercial glass containers during thermal processing. *Food Technol.*, **4**, 411 (1950).
2. Townsend, C. T., Reed, J. M., McConnell, J., Powers, M. J., Esselen Jr., W. B., Somers, I. I., Dwyer, J. J., and Ball, C. O. Comparative heat penetration studies on jars and cans. *Food Technol.*, **3**, 213 (1949).

Notes and Letters

Cooling of Cans

In a review of some Japanese work, published in Food Technology in October 1947, Olson *(4)* quoted some data of Okada *(2, 3)* on the cooling of cans. Film coefficients of 2.6 x 10^{-5}, 2.7 x 10^{-5} and 7.5 x 10^{-5} cal./cm.^{2} sec. ° C. were quoted for the cooling of cylindrical cans in air. These are equivalent to 0.19, 0.20 and 0.55 BTU/ft.^{2} hr. ° F. which seem incredibly low values. From general experience in heat transfer problems, a coefficient of the order of 2 BTU/ft.^{2} hr. ° F. would be expected. In his second paper *(3)*, on rectangular cans, Okada quoted values about 5.0 x 10^{-4} cal./cm.^{2} sec. ° C., or 3.7 BTU/ft.^{2} hr. ° F., a surprisingly high figure.

On obtaining a translation of this paper, kindly supplied by Mr. E. H. Flint of the University of Queensland, I found that Okada had derived his values from an incorrect form of solution of the equation of conduction of heat.

Okada used data on the heating and cooling of various fish packs, many containing a good deal of free liquid and some of them apparently having very large headspaces.

There are a number of reasons why calculations based on the equation of conduction of heat may give inaccurate results in such cases. Among them are:

1. That the equation will not apply exactly to packs containing a good deal of liquid,
2. that the film coefficient will not be constant but a function of the temperature differences, and
3. that it is sometimes difficult to make a simple assumption about heat flow in the head space which is a good approximation.

Okada treated his packs as cylinders or rectangular solids of the dimensions of the can, which is equivalent to assuming that the head space has the same thermal diffusivity as the fish pack. This assumption is not exact. It does not seem to lead to serious errors with the commoner types of cylindrical can in which radial heat flow is faster than vertical, but it is likely to be misleading for shallow cans with large head spaces. In some of the shallow rectangular cans studied by Okada the equations indicate surprisingly low thermal diffusivities (between one third and one half that of beef muscle). These are probably due to the unsatisfactory assumption made for the headspace.

While the assumptions made by Okada are likely to lead to more or less inaccurate results it is not easy to find simple ones which will be more exact. I have therefore recalculated some of his data using the same basic assumptions but correct solutions of the equation of conduction of heat as given by Carslaw and Jaeger *(1)*.

For cylindrical cans, approximately 215 x 404, nine sets of data gave film coefficients in air ranging from 1.8 x 10^{-4} to 2.3 x 10^{-4} cal./cm.^{2} sec. ° C., the coefficients increasing regularly with decreasing apparent thermal diffusivity. The apparent diffusivities ranged from 1.48 x 10^{-3} to 2.70 x 10^{-3} cm.^{2}/sec.

Film coefficients were also calculated for 18 packs in rectangular cans of various sizes, in all of which the height was the smallest dimension. As would be expected, these results were less consistent than those for the tall cylindrical can. The actual values varied from 1.3 x 10^{-4} to 7.8 x 10^{-4} cal./cm.^{2} sec. ° C. with a median value of 2.4 x 10^{-4} cal./cm.^{2} sec. ° C.

From these figures the most probable value of the film coefficient in air seems to be about 2 x 10^{-4} cal./cm.^{2} sec. ° C., or about 1.5 BTU/ft.^{2} hr. ° F. The film coefficient in still water indicated by Okada's data is about ten times that in air.

These coefficients are appropriate for the calculation of the cooling of freely exposed cans; they would not be reliable for calculating the cooling of cans inside a large stack in air.

E. W. Hicks.

December 13, 1950.

Commonwealth Scientific and Industrial Research Organization,
Division of Food Preservation and Transport,
Homebush, N. S. W., Australia.

LITERATURE CITED

1. Carslaw, H. S., and Jaeger, J. C. Conduction of heat in solids. Oxford University Press, 1947.
2. Okada, Mituyo. Cooling of canned foods. Japan Soc. Scientific Fisheries, *Bull.* **9**, 64 (1940).
3. Okada, Mituyo. Cooling of rectangular food cans. Japan Soc. Scientific Fisheries, *Bull.* **9**, 208 (1941).
4. Olson, F. C. W. Recent Japanese researches on canning technology. *Food Technol.*, **1**, 553 (1947).